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INDUSTRIAL SOLVENTS

BY

IBERT MELLAN

Industrial Chemist and Consultant

2nd ed.

SECOND EDITION

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TO ELEANOR

WIFE AND CO-WORKER

PREFACE TO SECOND EDITION

Eleven years have elapsed since the original publication of this book. During that time much progress has been made not only in the manufacture of solvents but in the development of new uses for them. It is not pretended that this book is completely inclusive of all the information that could ideally be desired in this wide ranging field. Its purpose is to gather together and organize for ready reference sufficient material about the more important solvents to enable the reader to find useful information between the covers of one volume, to save him the trouble of searching through the voluminous literature which has grown up around the subject.

The original scheme of the book has been generally adhered to, although several changes have been made in response to suggestions and criticisms from the field. It has been thought advisable to eliminate the chapter on Plasticizers with a view to eventually publishing this material as a separate volume. The chapter on Graphic Expression and Interpretation has also been eliminated. On the other hand, an entirely new chapter on the Safe Handling of Solvents has been added and selected bibliographies have also been included. Every effort has been made to check the accuracy of the statements given, and it is hoped that the present edition will be a great improvement over the first one in every respect.

Grateful mention should be made of the assistance rendered the author and the publisher by various individuals of Carbide and Carbon Chemicals Corporation, Commercial Solvents Corporation, Dow Chemical Company, E. I. Du Pont de Nemours & Company, Inc., American Cyanamid & Chemical Corporation and Hercules Powder Co. for helpful critical comments and for permission to utilize material originally developed by their research staffs.

It is the author's hope that the Second Edition will be accorded an even more favorable reception than the first and he solicits criticisms and suggestions from users of the book as to its possible improvement for a future edition.

IBERT MELLAN

New York, N. Y.
October, 1950

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Chapter 1

The Nature of Solution

Solution is everywhere: in the gaseous, the liquid, and the solid states. The air is a gaseous solution of nitrogen, oxygen, carbon dioxide, water vapor, argon, and other rare gases. The oceans are liquid solutions of chlorides, carbonates, and sulfates of sodium, magnesium, calcium, etc., in water. They actually contain about 32 of the known elements, including gold, and in every 1000 parts of sea water there are about 27 parts of sodium chloride. Ordinary tap water is a dilute solution of sodium, calcium and magnesium carbonates, sulfates and nitrates, dissolved ammonia, and carbon dioxide. The earth's crust, or lithosphere, consists of thousands of cubic miles of solid solutions: whole mountain ranges, great hills and uplands of granite, are solutions of metal, silicon and oxygen; limestone peaks, chalk downs and beautiful marble are solutions of calcium, carbon and oxygen, with oxides of iron and other metals as coloring agents.

A solution may be defined as a mixture of two or more substances which has uniform chemical and physical properties throughout. It may also be defined as a system whose component parts are two or more molecular species, there being no boundary surfaces between these parts larger than molecules. There are two components to every solution—the solvent and the solute. As a matter of convenience we designate the part of a solution which is in excess as the *solvent*; the solute is the component which is in smaller proportion. The composition of a solution may be expressed in several ways: a *molar* solution (or formal solution) contains 1 mole of a solute in a liter of solution; a *molal* solution contains 1 mole of a solute in 1000 grams of solvent; a *normal* solution is one which contains 1 gram-equivalent weight of a solute in 1 liter of solution. The solubility of a substance may also be expressed in percentage, as weight in volume or weight in weight.

The creation of life and its very existence depend upon solution. The ancient philosophers, recognizing its profundity, speculated on the mysteriousness of the nature of solution. This enigma has been studied from the early Egyptian era until the present time, and yet we know of no general principle by means of which the solubility of a substance can be predicted. Our theories of chemistry and of solution originated in antiquity. The remote Egyptian thinkers, as recorded in their cosmogonic myths, regarded water as the prime substance and the solid earth as the crystallized emergence from this solution. These ancients, however, as well as the early alchemists, were absorbed with the *modus operandi* of solution rather than with the nature of solution itself.

In more recent times, as science reached far beyond its early boundaries, investigators delved deeper into the chemistry of matter, reaffirming the early convictions that solubility and solution are of prime importance. The fact that chemical reactions result when a substance is dissolved in a liquid such as water, was recognized early, and an unrelenting search for the miraculous solvent that would dissolve everything was undertaken. Out of this search came the hypothetical solvent called the "Alcahest" by Paracelsus (1493–1541), which was regarded as "the philosopher's stone" or the "elixir of life".

The atomic theory, first proposed by Democritus of Abdera (460–362 B.C.), occupied the attention of the alchemists from the Alexandrine Greeks and Arabs to those of the Middle Ages; they hoped to transmute base metals into noble metals. Democritus advanced the astonishingly modern idea that matter consists of discrete atoms with empty spaces between them. Plato advanced the first fundamental theory of solution by teaching that the atoms of one substance may enter into the interstices between those of another substance. Aristotle, by opposing the atomic doctrine, laid a good idea to rest for about 2000 years.

Gassendi (1592–1655) took up the atomic theory again and elaborated upon it. He asserted that atoms could unite to form molecules and that solution results when a substance goes into the pores of a solvent. Newton (1642–1727) added a new conception to the world's knowledge of solution by advancing the theory that there is an attraction between the solvent and the solute. Boerhaave went further than Newton by assuming that both the solvent and the dissolved substance were in such an intimate relation with each other that the particles of each combined to form a new homogeneous substance. This union of solvent and solute was not in his opinion a mechanical one nor one that resulted from some strong repelling force, but rather a natural mutual attraction. Thus both Newton and Boerhaave established the significant fact that a resemblance exists between solution and chemical action, in that each is the result of a chemical union.

Wallerius' contribution to the theories of solution brought the eighteenth century to a close. He believed that the attraction between solvent and solute could be attributed to the fact that there existed a similarity between solvent and solute, and the stronger the similarity the greater the attraction between them. However, his contribution is valued chiefly for the stress he placed upon the fact that there is a *chemical affinity* between the two components of a solution.

Lavoisier in 1789 distinguished between solution and dissolution. He considered a solution to be a mechanical mixture. He assumed that there was no decomposition when salts were dissolved in water or when resins were dissolved in alcohol or other spiritous solvents, since both solvent and solute can be recovered. However, dissolution resulted in solutions of metals, where decomposition took place as the metal became oxidized. Fourcroy held this same theory, *i.e.*, that a solution is a physical phenomenon in which the solute is finely distributed throughout the solvent. Klaproth believed in a chemical affinity between solute and solvent which he stated was stronger than the cleavage of particles within the solute and the solvent. According to Berthollet, a solution is the result of a force greater than the cohesion of the solute. Solutions that were stable were called "combinations" and those that were less stable "dissolutions". Thus he considered solution to be a true chemical combination, and the difference between a solution and a chemical compound to be only in the firmness with which the parts are held together. In a solution the solute and solvent are not as securely united and each can be recovered. However, he believed that the same laws governed solution and chemical union.

J. J. Thomson in his "System of Chemistry" regarded solution as a chemical process. In 1808 Grotthus, known for his contributions to electrolysis, presented his view of this chemical process by stating that it was a manifestation of the phenomenon of galvanic electricity. Thus we come to the theory of solution held by the great Swedish chemist Berzelius, in which he viewed the phenomenon of solution as differing from a chemical union in that it took place without an "electrical act". He regarded solution as the result of some unknown form of mechanical affinity which was different from true chemical affinity. In other words, the forces which effect solution differ from those which bring about a chemical union; the substance dissolved is the same, but in another state of aggregation.

Gay-Lussac in 1839 recognized the important truth of the relationship between matter in liquid and gaseous solutions. He believed that solution is brought about by a force acting between the solvent and the solute. Williamson, the English chemist wrote a significant section in his paper of 1851 "On the Theory of Ether Formation", which proved to be another milestone in the development of our understanding of solution. He visualized the component parts of a solution as being in a constant state of movement as well as in a state of dissociation. The physicist Clausius took exception to Williamson's theory of dissociation by claiming that a solution consists chiefly of "whole molecules" with only a few "part molecules". Thus his contribution led to the development of the theory of electrolytic dissociation.

Many investigators continued to add to the sum total of our knowledge of solution. Some of the more outstanding were Guldberg and Waage, who gave us the law of mass action; Valson, who conceived the "law of capillary module"; Gladstone, with his work on refractivity of solutions; and Kohlrausch, who worked on the measurement of conductivity. Berthelot, Thomson, Raoult, Mendeleeff, and Arrhenius brought to a close an era which concerned itself with the study of solutions in which epoch-making generalizations were formulated. Arrhenius and his work on electrical dissociation ushered in a period in which scientists such as Traube, Pfeffer and Van't Hoff worked out methods which proved the magnitude of these hypotheses. Traube measured osmotic pressure, and Van't Hoff worked upon the relation between solutions and gases.

Investigators have observed that "like dissolves like" and that a solvent usually dissolves substances which are analogous to it in chemical composition. Thus from the properties of a substance, it is possible to predict with certainty whether or not it will dissolve in a particular solvent. We know that solubility depends upon the properties of both the solute and the solvent and that the process of solubility is mutual. The conception that "like dissolves like" is represented in the theory in which solvents are divided into two groups. In the first group the atoms are of such a nature that they do not set up electrical stresses across the molecule; therefore, no residual valence forces are present. The second group is composed of molecules whose atoms or atomic groups do set up electrical potentials. The first group is known as *nonpolar* solvents, for example, the hydrocarbons; the second group comprises the *polar* solvents, an example of which is the oxygen-containing solvent, water. Thus we find that the substances which most readily dissolve in the nonpolar solvents are themselves nonpolar in nature, and those which are freely soluble in polar solvents are polar.

Coltof[1] studied the solubility properties of certain highly polymeric substances, paying special attention to the phenomenon of dissolution in regard to dispersion, swelling and ballast action. He observed that when a highly polymeric substance is attacked by a solvent, the primary phenomenon is swelling. The swollen material grows and changes into a gelatinous mass and ultimately becomes completely miscible with the solvent. This observation is true only when solution is complete, while in other instances only a limited swelling occurs. The following is a summary of his findings:

"(1) There are two kinds of interaction between a liquid (simple or mixture) and a highly polymeric substance: (a) miscibility in all proportions (resulting in a solution or in a jelly, according to the fluidity of the mixture); (b) limited swelling (part of the liquid being absorbed by the swollen substance, while a certain part of the substance passes into the remainder of the liquid).

"(2) Miscibility in all proportions is the only important form of interaction from the technical point of view.

"(3) To attain miscibility in all proportions it is necessary for the solvent to effect dispersion and swelling in a certain ratio and to such an extent as not to be impaired by the ballast of the solvent molecule.

"(4) Each atom grouping of a solvent molecule exerts a dispersing, a swelling, and a ballast action to a certain extent, dependent on the nature of the substance to be dissolved and the temperature. The effect of the molecule is the result of the specific actions of its groups.

TABLE 1.1. SPECIFIC ACTIONS OF SOLVENT GROUPS TOWARD DIFFERENT HIGHLY POLYMERIC SUBSTANCES[1]

SOLVENT GROUP	SUBSTANCE TO BE DISSOLVED		
	Cellulose acetate	Ethylcellulose	Chlorinated polyvinyl chloride
$\cdot C_2H_5$	Ballast	Chiefly swelling	Ballast
$\cdot C{:}C\cdot$	Swelling	Swelling and dispersion	Swelling and some dispersion
$\cdot Cl$	Chiefly ballast	Chiefly ballast	Swelling and some dispersion
$>C{:}O$	Swelling and dispersion	Dispersion	Dispersion
$\cdot OH$	Dispersion	Dispersion	Ballast

TABLE 1.2. DISPERSING AND SWELLING ACTION OF ORGANIC LIQUIDS TOWARD CHLORINATED POLYVINYL CHLORIDES[1]

	METHYL ALCOHOL	ACETONE	*n*-BUTYL ACETATE
Dispersion	0	4	3
Swelling	0	1	2
Sum	0	5	5
Ratio	—	4:1	1½:1

	BENZENE + ACETONE 5:1	TETRACHLOROETHANE	BENZENE	CARBON TETRACHLORIDE
Dispersion	4	5	2	1
Swelling	3	5	3	4
Sum	7	10	5	5
Ratio	1⅓:1	1:1	1:1½	1:4

"(5) The combined effect may also be obtained by applying a suitably composed mixture of liquids.

"(6) Heating tends to increase dispersion and to decrease swelling.

"(7) In the case of highly polymeric substances having two characteristic groups, the ratio between these groups often determines the required ratio between dispersion and swelling groups of the solvent.

"(8) It is impossible to express the solvent power of a liquid (simple or mixture) towards one or more highly polymeric substances in a reliable way by means of a quantity which is a function of physical constants of that liquid."

Some of the newly developed solvents have several functional groups for the purpose of increasing their range of solvent action. The presence of an (OH) group imparts the characteristics of water or an alcohol; a —C·O·C— group gives the characteristics of an ether; a —C:O group the properties of a ketone.

Doolittle[2], who has made many contributions to the science of organic solvents, has made a study of the mechanism of solvent action which should be studied in full. However, only a brief abstract of his researches, as well as his summary, is included here.

"Two principal equilibria are simultaneously operative in the solution of resinous substances—solvation-desolvation and aggregation-disaggregation. The rate of desolvation is substantially fixed at constant temperature, but the rate of solvation is a function principally of solvent concentration. The threshold concentration required to initiate the solution process diminishes to a constant minimum value as we ascend a homologous series of solvents. This minimum value, called 'class threshold concentration', is independent of the diluent and therefore serves as an absolute comparison of different classes of solvents for a given resinous substance. The aggregation-disaggregation equilibrium of the solute macromolecules depends on the solvation-desolvation equilibrium, since disaggregation results when the 'active centers' are solvated. In fluid solutions the extent of aggregation of the solute macromolecules increases linearly with decrease in solvent concentration; but as solvent concentration approaches the threshold value, desolvation permits aggregation at multiple points of contact. The result is either gelation or precipitation. In film formation, the high viscosity, resulting from aggregation by means of gradual two- and three-dimensional growth as the resin desolvates during evaporation of the solvent, obstructs the tendency of the macromolecules to unite with one another at the maximum number of points of contact. A rather extended structure results. Plasticization prevents complete desolvation of the resin, and therefore diminishes the opportunity of the macromolecules to unite with one another at multiple points of contact. In this manner a less rigid structure is provided.

"1. In homologous series of solvents the mole concentration of solvent at the dilution ratio end point, called the 'threshold concentration', n_{DR} approaches a minimum value as the molecular weight of the solvent increases. This minimum is independent of the diluent used, provided only that the diluent is truly a non-solvent, and is an indication of the relative effectiveness of each class of solvents for a given macromolecular substance.

"2. Since the lower molecular weight solvents of a given class are less effective per mole of solvent than higher molecular weight members, it is possible in certain instances to pass out of the solvent region on the low molecular weight side of the series. It is always possible, however, to pass out of the solvent region on the high molecular weight side because the mole concentration of solvent required to initiate the solution process approaches a fixed minimum value whereas the mole concentration of the pure solvent diminishes continuously as the molecular weight increases.

"3. The logarithm of the relative viscosity of resin solutions of fixed solids content is approximately linear with the reciprocal concentration of solvent except in the neighborhood of the reciprocal threshold concentration, $1/n_{DR}$. In this region the viscosity increases rapidly, the curve becoming asymptotic to $1/n_{DR}$. Thus, the threshold concentration may be experimentally determined by either dilution ratio or viscosity methods.

"4. The experimental evidence is interpreted in the light of the author's point of view in regard to the mechanism of solvent action, and further conclusions are drawn in regard to film formation and plasticization."

Evans and Young[3] have studied the solubility of polybutene in sixty pure solvents. It is their conclusion that polybutene is insoluble in the low molecular weight alcohols and that the solubility increases as the molecular weight of the alcohol is increased.

It is interesting to contrast the theory of Barr and Bircumshaw[4] with that of Byron[5]. The former claim that the solution of nitrocellulose in a mixture of alcohol and ether is explained by the fact that alcohol polymerizes in the presence of ether and is then a solvent for nitrocellulose. Byron is of the opinion that alcohol is not polymerized but is dissociated, and that ether in this case aids in this dissociation. It is Esselen's[6] theory that the increased solvent action of a mixture of chloroform and alcohol for cellulose acetate is due to the adsorption of the hydroxyl groups within the cellulose molecule which leaves the acetate groups covered with alcohol groups. In the opinion of Mardles[7], solvent liquids are attracted to cellulose esters and form complexes with them. McBain[8] agrees with Mardles in respect to these complexes, but goes further in pointing out the fact that, in the solution of cellulose esters in a mixture of solvents, different solvent molecules are attracted to different portions of the solute.

Atoms are made up of aggregates of electrons, protons, and neutrons. The first two are units of negative and positive electricity; neutrons, as the name implies, are electrically neutral. The number and groupings of these units determine the chemical properties and the nature of the element. All substances are made up of atomic and molecular aggregates, and their character is governed by the arrangement and number of these. To take polymerized acetone as an example, it can be said to contain aggregate acetone molecules, atomic aggregates, and electron-proton-neutron aggregates or, graphically, there are aggregates of aggregates of aggregates. Molecular aggregates are formed by groups of atoms and molecules which attract one another and hold together by borrowing and lending electrons, which are internal electrical forces called secondary valences. These structures are conveniently called "molecular aggregates" and serve as the structural unit for the theory of solvent action.

Postulates

1. A liquid may or may not form molecular aggregates. Any liquid which dissolves and ionizes holds greater possibilities of forming aggregates. This is explained by the fact that the dissociated groups are attracted to each other and are held together by the passage of one or more electrons from one atom to another. These are known as *polar compounds*. If a substance is a nonpolar compound, there is little or no dissociation, and therefore aggregates are formed in lesser quantities. These aggregate groups are held together by electrostatic union, that is, a union of two or more groups established by sharing in common one or more electrons. According to Turner[9], the tendency to aggregation in organic compounds is due to the presence of certain electronegative groups. For example:

OH ⟨ Alcohols
Phenols
$CONH_2$ ⟨ Amides
Anilides
$COOH$—Carboxylic Acids
NOH—Oximes
CN—Nitriles
SH—Mercaptans or Sulfhydryls
$CSNH$—Thioamides
$CSOH$—Thioacids
NH_2—Primary Amines
NO—Nitrocompounds
CHO—Aldehydes
CO—Ketones

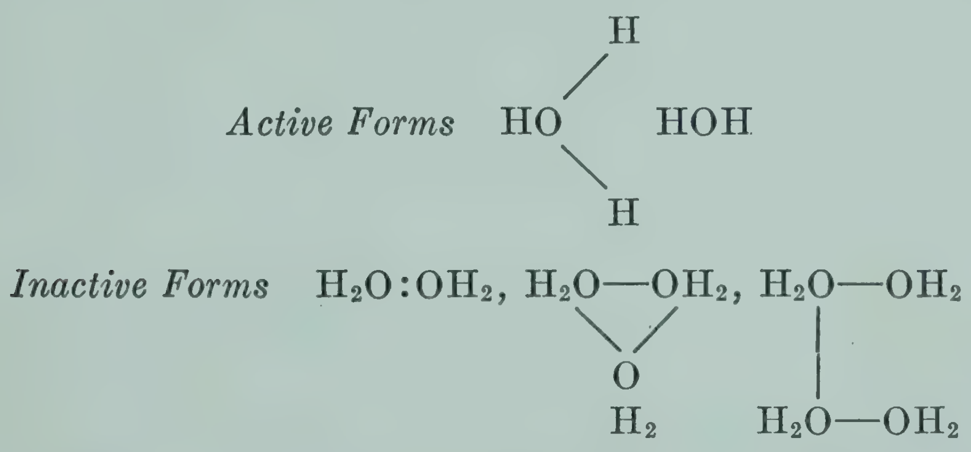
The influence of these groups decreases in the order given. Factors which govern molecular aggregate formation are the mass, its structure, and the groupings in a molecule. The tendency which leads to molecular aggregation decreases with an increase in molecular weight within the homologous series.

2. A mixture of two or more liquids may or may not form one or more molecular aggregates. When liquids are admixed there is often seen an abnormal change in volume, notably a shrinkage in volume when water and ethyl alcohol are mixed together. This is explained by the fact that molecular aggregates are formed. The evolution of heat or the adsorption of it when solution takes place indicates aggregate groupings. This heat exchange is the result of forces acting between or among the molecular groups.

Changes in specific gravity are evidences of molecular aggregate formations at different concentrations. These physical changes can be observed when water is mixed with either ethyl alcohol, propyl alcohol, formic, acetic or propionic acids, or acetone. Turner[9] has observed maximum deviations in volume when the following are mixed in the proportions of one molecular weight of ether to one of alcohol; two of benzene to one of ether; and one of ether to two of chloroform.

3. A liquid plus a solid may or may not form one or more molecular aggregates. Turner declares that substances containing the following groups produce the most abnormal results in the order given: hydroxyl, carboxyl, amino, aldo, cyano, ester, nitro, iodide, bromide, and chloride. Worden[10] records certain types of cellulose ethers which are insoluble in both hot and cold water. When water is frozen and permitted to thaw gradually, the liquefied water will then dissolve the cellulose ether. This clearly shows that proper conditions have been brought about for the rearrangement of the molecules into such groups which exhibit solvency for the particular type of cellulose ether. We can go further and say that liquids which under ordinary conditions exhibit little or no solvent power can be altered by admixture with other solvents or changed by physical means, thus bringing about the formation of molecular groupings which possess specific solvent power.

Armstrong[11] attempted to explain the phenomena of water aggregates by simple molecules, chain and ring formations:



4. If we mix liquid *A* with liquid *B* and no molecular aggregates are formed we say that the two liquids are insoluble in each other or that they are immiscible. If a small amount of *A* is taken up by *B* then the molecular aggregates formed are of the type which contains many whole or part molecules of *B* to few of *A*. The structure can be calculated from the size of the molecule, number per cubic centimeters and the degree of solubility. This assumption is true if only one type of molecular aggregate is formed.

But how can we determine if one or more aggregates are formed? This is possible by x-ray diffraction patterns. It is known that liquids of different chemical composition have different diffraction patterns. It has also been shown that two liquids which are completely miscible show a diffraction pattern different from that of either of the constituents. Two liquids which are not miscible at room temperature show individual diffraction patterns.

5. If a larger amount of *A* is taken up by *B*, then the ratio between the

A and *B* molecules in the aggregate is smaller, and the possibility of forming more than one type of molecular aggregate is greater.

6. Solubility is the formation of molecular aggregates. The degree of solubility will depend upon the type or types and number of molecular aggregates formed. Temperature exerts its influence on the type and number of aggregates formed which in turn governs the degree of solubility. For example, if a small quantity of alcohol is taken up by benzene from a dilute alcoholic solution, the molecular aggregates produced contain many benzene molecules to few alcohol molecules and the number of different resulting aggregates is few. In the case of alcohol and water, where many types of molecular aggregates are formed, the ratio between the alcohol and water molecules and the dissociated groups in the aggregates is a simple arithmetic relationship.

7. Miscibility, like solubility, depends upon the internal electrical attraction of atoms, molecules, or groups of these, with the formation of molecular aggregates. Complete miscibility means that all the molecules of the different liquids form one or more groups of molecular aggregates. Molecules of liquids that repel each other with an electrical force will not mix or dissolve, and are called *immiscible* liquids. If a mixture contains three or four liquids, the possibility of forming one or more molecular aggregates is consequently greater. Mixed solvents behave like more complex solvents of the ester or alcohol-ether type. In the former, the groups are held together by secondary valences and in the latter, they are bound more firmly by primary valences.

Meyer[12] has found that the ionization diffraction curves of two organic solutions change with the concentration. When short-wave radiations were used on mixtures of normal butyl alcohol with orthodiethyl-cyclohexane the diffraction peaks shifted from the peak of one member to the peak of the other as the concentration changed from 100 per cent of one member to 100 per cent of the other, and the width of the peak varied in the same manner. It has been shown by a number of workers that the diffraction curves and peaks indicate groupings of the molecules and the spacing is governed by the constituent parts. These spacings can actually be approximated by Bragg's law.

8. A case where large molecular aggregates are formed: If a small amount of *A* is added to *B*, the molecular aggregates formed contain many *B* molecules and few of *A* molecules. This condition results in fewer molecular groups per volume with a corresponding rise in both the freezing point and the vapor pressure temperature. This assumption is verified by the experiments of Wright[13], who discovered that the addition of a large amount of alcohol to benzene forms alcohol-benzene complexes which bring about a lowering of the freezing point. This condition is the result of the formation of alcohol, alcohol-benzene, and benzene aggregates. If water is added to this mixture, water-alcohol aggregates are formed. This is explained by the fact that the water and alcohol molecules have greater attraction for each other than do the alcohol and benzene molecules. Thus, in this mixture, most of the benzene molecules are set free from the alcohol-benzene groups. The liberated benzene contains a small amount of benzene-alcohol aggregates, which causes a rise in the freezing point of the liberated benzene. Wright's experiments reveal the fact that when a solute which is more soluble in alcohol is added to a binary mixture of alcohol and benzene (50%-50%) there is, at first, a rise in the freezing point. Upon adding more of this solute, a depression of the freezing point is brought about. When a solute more soluble in benzene is added to this same mixture a lowering of the freezing point is obtained.

Solutes which produce a rise in the freezing point form molecular aggregates which contain large numbers of molecules. Thus a condition is created in which we have fewer molecular aggregate groups per given volume. In higher concentrations the molecular aggregates are broken down into smaller groups which produce a larger number of molecular aggregate groups per given volume, and this consequently produces a lowering of the freezing point. When solutes are added which are more soluble in benzene than in alcohol, many small molecular aggregates are formed; these increase the number of groups per given volume and thus cause a depression of the freezing point. Following this line of thought, we can mix specific solvents in given proportions to form molecular aggregates in which there are no free molecules of the individual solvents. Such mixtures should possess a constant freezing or boiling point and should exhibit diffraction patterns peculiar to their type. Going further, if an excess of one solvent is added to this constant boiling point mixture, the state of equilibrium is upset and we no longer have the condition of constancy.

In another experiment, Wright added a small amount of water to an alcohol-benzene mixture (50%-50%) until the solution became turbid. The addition of sodium chloride to this turbid mixture caused it to become clear. According to the theory of molecular aggregates, the alcohol molecules in the alcohol-benzene group have a greater attraction for the water molecules than for the benzene molecules; they therefore leave the benzene and unite with the water. The liberated benzene is dispersed in this mixture and causes it to become turbid. With the addition of sodium chloride we introduce a substance which possesses greater internal electrical attraction for the water molecules and therefore pulls them away from the alcohol and finally unites with them. The liberated alcohol and the previously liberated benzene are now free to attract each other and to form molecular aggregates, with consequent clearing of the solution.

9. An attraction exists between or among the appropriate groups of solute and solvent results in solution.

10. Where mixed solvents are concerned the increase in the number of different solvent groups increases the number of solvent-solute aggregates; this results in increased solubility.

11. If, in place of attraction there is repulsion, the condition of insolubility, immiscibility or precipitation is produced.

12. Brown and Bogin[14] have pointed out that the boiling point of a liquid has no relation to its volatility. It therefore can be assumed that the boiling point is the temperature at which the vapor pressure of molecular aggregates is equal to the atmospheric pressure. On the other hand, volatility depends upon the type of molecular aggregates present. These investigators also found that though there is only 2° C difference in boiling points between toluene and isobutyl alcohol, the former will evaporate almost three times as rapidly as the latter. Another example is that of xylene and normal amyl acetate which boil at practically the same temperature; but the hydrocarbon evaporates 1.25 times as rapidly as the ester. Butanol boils 22 degrees below xylene but it evaporates only about 80 per cent as rapidly. These differences in evaporation rate are due to molecular aggregation and are governed by the force of the internal attractions or secondary valences. These workers state that vapor-pressure curves are a more accurate means of solvent evaluation than is a study of boiling points, but that they are of assistance only insofar as they lead to a better understanding of the principles governing evaporation; and that "the only sectors of vapor pressure curves that are of practical interest are those temperature ranges that represent normal room conditions." Two solvents with identical vapor pressures will evaporate at different rates at a given temperature unless their molecules are of the same weight and their latent heats of evaporation are identical. The solvent with the greater molecular weight will evaporate more rapidly. From the above we can conclude that the latent heat of evaporation is the energy (heat) needed to break the secondary-attraction bonds in the molecular aggregate and to supply the energy in the newly formed aggregates.

Mixtures of solvents may form binary, ternary, quaternary, or polynary vapor-pressure mixtures of a complex nature. A state of equilibrium is never reached except that which exists at a given temperature. This is because, as evaporation goes on, energy (heat) is consumed and there is a constant lowering of temperature. For example, the rate of evaporation of a mixture of 30 per cent benzene and 70 per cent ethyl alcohol, at room temperature, is about 25 per cent more rapid than the rate derived from the formula for the evaporation of the "perfect mixture."

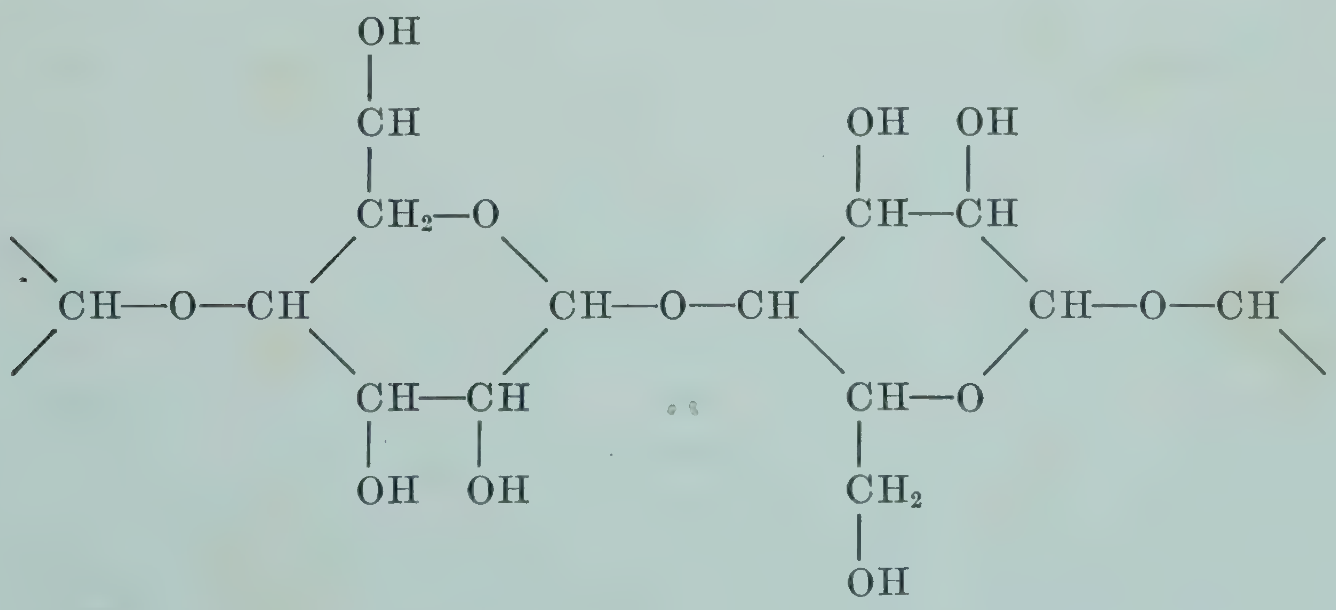
In constant-boiling mixtures there is a predominance of one type of molecular aggregate, and the ratio between the constituent parts in the aggregate always remains the same during the process of evaporation.

Lacquer imperfections—for example, cotton blush, gum blush, improper drying rate, orange peel, poor flow, water blush and so forth,—are believed to be due to improper balance of the evaporation rates of the solvents and diluents. These imperfections are in reality due to the formation of undesirable molecular aggregates possessing nonsolvent qualities.

The researches of Jean-Jacques Trillat[15] dealing with the change of lattice structure of nitrocellulose prove the presence of crystalline aggregates made up of nitrocellulose (12.9% nitrogen) and acetone. The presence of these compounds has also been confirmed by means of x-ray spectrography. With this new scientific instrument, it is possible to see the formation of more than one crystalline compound when an acetone solution of nitrocellulose is going through the process of drying. Similar compounds are formed when ethyl acetate is used in place of acetone, with corresponding variations in the lattice structure. When dissolvents with less solvent power are used, these phenomena become less clear and almost disappear. Lattice pictures of cellulose show secondary valences as feeble linkage forces, and the glucose groupings in the cellulose are bound together by primary valences.

Molecular aggregates are formed by the union of cellulose ester, solvent, and plasticizing molecules. It has been shown that the structure of regenerated cellulose ester films varies with the ester, solvent and plasticizer used. This is in accordance with the theory of the formation of molecular aggregates. Further, as a solvent leaves a molecular grouping by evaporation, the remaining constituent parts exert their individual force, which results in new groupings with different lattice structures. Lacquer films are structurally made up of cellulose molecules randomly oriented with resin and plasticizer which fill in the interstices.

Cellulose is made up of hexose groups linked together by oxygen bridges. The chain, comprised of bundles, is united by secondary-valence forces. X-ray measurements confirm the general belief that cellulose is built up of parallel chains of "glucose residues" linked by oxygen atoms.

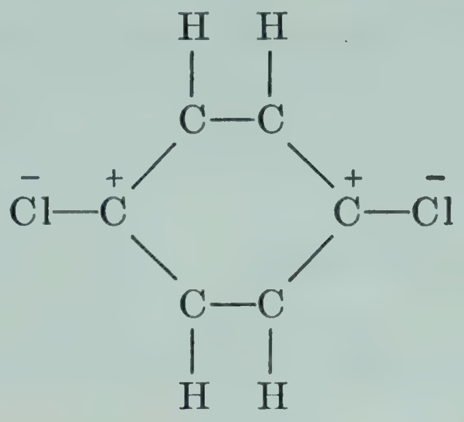


In nitrating cellulose the hydroxyl groups (OH) are attacked and nitrocellulose is formed. When this is dissolved in a solvent, molecular groups in chain formation result. The length of the chain depends upon the concentration and dissolvent power of the solvent or solvents. Dilute solutions and good solvents yield small chains free to move about in the solvent phase of the solution. Extremely dilute solutions contain the solute subdivided into individual molecules. These chains form molecular aggregates with the solvent, resin and plasticizer, with the provision, of course, that these are of the right type.

Baker[16] believes that the decrease in viscosity of an ether-alcohol solution of collodion is caused by the formation of an ether-alcohol complex and that this complex is responsible for the solvent action of nitrocellulose. Byron[5] has discovered that pyroxylin is not peptized by anhydrous ether but by absolute alcohol at low temperatures, which permits his assumption that when alcohol is added to ether it becomes polymerized and is the causative agent in the solution of pyroxylin.

Polar and Nonpolar Compounds

Water is not by any means the only solvent which has electrical conducting properties caused by the dissociation of dissolvent substances. Liquid ammonia, liquid sulfur dioxide, and liquefied hydrocyanic gas possess this property in the same degree as water. Many organic solvents, like alcohols, acids, aldehydes, nitriles, amines and so forth, exhibit this conductivity. These substances are chemically active and are referred to as "polar solvents." Compounds which are comparatively inert, such as the hydrocarbons and their derivatives, *e.g.*, benzene, gasoline, kerosene, chloroform and carbon disulfide, are classified as nonpolar substances. Drummond[17] groups solvents as polar and nonpolar by their high or low dielectric constants. Solvents like alcohols and ketones, which contain hydroxyl or carbonyl groups, have high dielectric constants, which is evidence of strong polarity. Those of low dielectric constant, like the aliphatic and aromatic hydrocarbons, are nonpolar solvents. Solvents in forming molecular aggregates, either within themselves or in combination with other solvents or solutes, exert polar action which is caused either by the dissociated solute or by the molecular aggregate formed. Rule and Mitchell[18] have found that "polar groups" exert an influence on the neighboring molecules which leads to changes in rotatory power. Rule and McLean[18] are of the opinion that the nonpolarity of some solvents may be due to the symmetrical arrangement of the substituent dipoles. Some molecules exhibit nonpolar properties with reference to a uniform external field. They may, however, exert a definite force on a point charge or dipole in their immediate neighborhood. In the carbon disulfide molecule the two oriented dipoles are so close to each other ($S = C^{++} = S$) that the field exerted by one, at a near-by point, is almost completely neutralized by the other. The polar properties of this compound, if they exist, will be extremely weak. In paradichlorobenzene, the C – Cl poles are separated by two carbon atoms and therefore function individually.



Paradichlorobenzene displays stronger polarity than does the monosubstituted product. Highfield[19] is of the opinion that the polarity of nitrocellulose is due to the presence of the strong hydroxyl polar groups and the weak polar hydrocarbon groups, and that there is a relationship between the hydroxyl content of nitrocellulose and its solubility in a solvent mixture containing a number of hydroxyl groups.

Dilution Ratio

A solution of nitrocellulose containing an active solvent will tolerate a definite quantity of nonsolvent, and the maximum amount is called the critical point. A further addition of nonsolvent will cause precipitation, or gelling, of the nitrocellulose. The aggregates which are formed between the solvent and the cotton derivative have some secondary-valence forces available for other substances, among which are nonsolvents. Some of these added substances naturally have greater attraction for the solvent molecule or aggregate than has the cellulose. If an amount of a nonsolvent, like benzene, is added just short of the critical point, it attaches itself to the solvent or solvent-cellulose aggregate and is held there by secondary-valence forces. This addition of benzene produces no visible change. If, however, an additional amount of nonsolvent is added which will make the volume greater than can be tolerated, precipitation will take place. This precipitation of nitrocellulose is due to the fact that the added nonsolvent benzene has a greater attraction for the aggregate than have the molecules of the cellulose derivative. This attraction ruptures the secondary-valence bonds between solvent and cellulose molecules and the benzene forms a new aggregate with the solvent.

The critical point, or limit of tolerance in a quantitative significance, is called the *dilution ratio*. It is a useful index which expresses the number of cubic centimeters of nonsolvent required to gel, or coagulate, some of the "½-second nitrocellulose cellulose" in 1 cubic centimeter of a solution of definite concentration. Factors influencing the results of dilution ratio tests are the types of solvent or solvents used, the types of nonsolvent or nonsolvents added, the type of nitrocellulose employed, the temperature of testing solutions, and the concentration of the nitrocellulose solution. Solutions of gums and resins in hydrocarbons or alcohols will tolerate only a definite quantity of added nonsolvent. Here, the amount of diluent which can be added also depends upon the above-mentioned variables. Dilution ratios can be empirically determined by the "dilution ratio method."

$$\text{Dilution Ratio}^{20} = \frac{Vd}{Vn} \text{ D. R.}$$

Vd refers to volume of diluent
Vn refers to volume of solvent

D. R. corresponds to the solvent-power number of Mardles[7] which is defined as the "volume of liquid (diluent) in cubic centimeters required to begin precipitation from 1 cubic centimeter of a 5/100 concentration sol." Thus, the "solvent-power number" and the "dilution ratio" represent the maximum quantity of a nonsolvent or diluent which can be added to a particular solution without producing undesirable effects. It does not, however, tell us anything about other important factors of a good practical lacquer, such as vapor pressure or rate of evaporation. Dilution ratios are useful in the fabrication of a lacquer or varnish, but are of no assistance in making predictions about the balance of solvents, diluents, resins, cellulose derivatives, and plasticizers during the period of drying. The dilution ratios of a number of solvents in various blends are given in Tables 1.3 and 1.4.

Diluents and Thinners

In lacquer formulation alcohols and esters of high boiling point are used to hold the nitrocellulose and the resin in solution. If a diluent or blending agent is needed, it too must possess a high boiling point to keep the proper volatility balance. The components of a solvent mixture may comprise such materials as coal-tar hydrocarbons, petroleum distillates, turpentine fractions, alcohols, ethers, esters, and ketones, depending on the kind of solution desired. Some of these substances are added not only to meet the demand for low-cost solvents and thinners, but also because their presence is often very necessary for complete compatibility. These so-called diluents are active solvents for certain resins such as rosin, elemi, mastic, dammar, ester gum, coumarone and synthetic resins, and are of value in blending these resins with cellulose derivative solutions. Their power to reduce the viscosity of a concentrated lacquer gives them the name of *thinner*. The resinous material added to lacquers imparts depth, adherence and gloss to the film, while the diluent effects flow and vaporization.

TABLE 1.3. Dilution Ratios of Various Solvents

SOLVENT	DILUENT										
	Mineral Spirits	Petroleum Naphtha	Toluene	Xylene	50% Toluene 50% Naphtha	Benzene	Aromatic Petroleum Diluent (42–50%)	Gasoline	Toluene 25% Gasoline 75%	Toluene 50% Gasoline 50%	Toluene 75% Gasoline 25%
Acetone		0.7	5.0	3.7	1.5		1.3				
Acetonylacetone				1.8							
Amyl acetate (commercial)		1.5	2.7		1.9				1.7	2.1	2.3
Amyl acetates (isomeric)		1.3	2.5	2.4	1.9						
sec-Amyl acetate		1.1	2.1	2.1	1.5		1.5		1.4	1.5	1.7
Amyl lactate		2.5	4.2								
Benzyl ether of ethylene glycol				3.0							
n-Butyl acetate	1.3	1.7	2.9	2.7	2.1	2.6	1.9				
sec-Butyl acetate		1.4	2.8	2.6	1.8	1.5	1.7				
Butyl butyrate		0.9	1.8	1.8							
Butyl ether of ethylene glycol	1.9	2.3	5.3	3.2	2.6	2.6			2.2	2.4	2.4
Butyl ether of ethylene glycol acetate	1.0			1.9							
Butyl ether of diethylene glycol	1.2			4.2							
Butyl ether of diethylene glycol acetate	0.6			1.8							
Butyl ether of propylene glycol		0.6	1.4	1.5		1.2			0.9	1.0	1.4
Butyl furate			3.8					1.4			
Butyl lactate	2.1	3.0	5.7	5.1	4.0						
Butyl oxybutyrate		2.2		3.8							
n-Butyl propionate	0.7	1.4	2.5	2.3	1.5				1.3	1.4	1.5
Cyclohexanone	1.0			7.5							
Cyclohexanyl acetate		1.4	2.5								
Diacetone alcohol (diacetone)	0.3	0.6	3.0	2.0	1.1		1.0	0.5			
Diamyl phthalate		2.0	2.2								
Dibutyl phthalate		1.7	2.7	2.6							
Dibutyl tartrate		1.4	8.0	7.7							
Dichlorethyl ether			S_1								
Diethyl carbonate		0.5	1.1								
Diethyl ether of ethylene glycol	0.2			0.4							
Diethyl ether of diethylene glycol	0.5			1.4							
Diethyl ketone		0.7	3.0								
Diethyl phthalate		0.7	3.8								
Diethylene glycol			S								
Diglycol diacetate				1.3			0.8				
Diisobutyl ketone	0.6		1.5	1.5							
Dimethyl phthalate			2.9								
Dipropyl ketone	0.3	0.9	3.1	2.7							

TABLE 1.3. *Continued*

SOLVENT	DILUENT										
	Mineral Spirits	Petroleum Naphtha	Toluene	Xylene	50% Toluene 50% Naphtha	Benzene	Aromatic Petroleum Diluent (42-50%)	Gasoline	Toluene 25% Gasoline 75%	Toluene 50% Gasoline 50%	Toluene 75% Gasoline 25%
Ethyl acetate		1.1	3.3		1.9		1.6				
2-Ethyl butyl acetate			2.1								
Ethyl butyrate		0.7	1.9								
Ethyl ether of ethylene glycol	0.7	1.1	5.3	4.3	1.8	4.8			1.6	2.6	4.5
Ethyl ether of ethylene glycol acetate	0.7	0.9	2.6	2.3	1.4						
Ethyl ether of diethylene glycol			S	1.2							
Ethyl ether of diethylene glycol acetate	0.6		2.2	1.9							
Ethyl ether of propylene glycol		0.8	2.8	2.8		2.7			1.3	1.9	2.7
Ethyl furate			3.5					0.7			
Ethyl lactate		0.7	5.5	4.7	2.5			0.8			
Ethyl oxybutyrate		1.3	4.5	3.7							
Ethyl propionate		0.8	2.1								
Ethylene dichloride			S_1								
Fenchone	0.8			2.9							
Furfural			2.9	1.6				0.2			
Furfuryl acetate			1.7	1.3				0.5			
Furfuryl alcohol				1.5							
Furfuryl furate			2.7					0.1			
Glycol diacetate				1.4							
Hercosol		0.1	0.4								
sec-Hexyl acetate	0.8			1.8							
Hexyl (2-ethyl butyl) acetate	1.1			2.0							
Isoamyl ether of ethylene glycol		1.1	2.4			2.2			0.5	0.7	0.9
Isoamyl ether of propylene glycol		0.4	1.4	1.4		2.4			0.6	0.8	0.9
Isoamyl furate			3.2				1.4	1.6			
Isobutyl acetate		1.1	2.7								
Isobutyl ether of ethylene glycol		1.6	2.0	2.0		1.5			1.1	1.3	1.6
Isobutyl ether of propylene glycol		0.3	1.5	1.3		1.2			0.5	0.7	0.9
Isopropyl acetate		1.3	2.7				1.7				
Isopropyl ether of ethylene glycol	1.3	1.6	4.3	3.8		3.2			1.5	2.3	2.5
Isopropyl lactate		1.2	5.0								
Mesityl oxide		0.9	3.8				1.9				
Methanol (anhydrous)		0.3	2.5								
3-Methoxybutyl acetate	0.9			2.1							

TABLE 1.3. *Continued*

SOLVENT	DILUENT										
	Mineral Spirits	Petroleum Naphtha	Toluene	Xylene	50% Toluene 50% Naphtha	Benzene	Aromatic Petroleum Diluent (42–50%)	Gasoline	Toluene 25% Gasoline 75%	Toluene 50% Gasoline 50%	Toluene 75% Gasoline 25%
Methylacetone		0.7	4.7								
Methyl acetate		0.9	2.3								
Methyl alcohol			2.5								
Methyl amyl acetate	0.8	1.0	1.7	1.6			0.9				
Methyl *n*-amyl ketone	1.1	1.2	3.9	3.6							
Methyl *n*-butyl ketone		1.1	3.9								
Methylcyclohexone	1.0			4.5							
Methyl ether of diethylene glycol			2.3	1.0							
Methyl ether of ethylene glycol		0.2	4.7	2.9		4.3			0.4	0.9	2.7
Methyl ether of ethylene glycol acetate	0.4	0.6	2.3	1.9							
Methyl ether of diethylene glycol acetate	0.3			1.7							
Methyl ether of propylene glycol		0.5	4.4	3.5		3.7			0.9	1.8	3.5
Methyl ethyl ketone		0.9	4.3	3.1	1.7		1.4				
Methyl furate			3.1					0.4			
Methyl *n*-hexyl ketone		0.9	3.6								
Methyl isobutyl ketone		1.0	3.5	3.7	1.9		1.6				
Methyl isopropyl ketone		0.9	3.6								
Methyl propyl ketone		1.0	4.0	3.4			1.8				
Octyl acetate		0.8	1.3								
Oxtyl (2-ethyl hexyl) acetate	1.0			1.4							
Phorone	0.7		2.2	2.2							
Propyl acetate	1.2	1.2	3.0	2.0	1.7						
Propyl ether of ethylene glycol		1.3	3.4	3.6		3.0			2.0	2.4	2.9
Propyl ether of propylene glycol		0.7							1.1	1.3	1.8
Propylfurate			3.9								
Propylene oxide			2.5								
Tetrahydrofurfuryl alcohol			7.8	2.6							
Tricresyl phosphate		0.7	3.2	3.5							

Mixing of solvents, diluents and thinners often results in change of solvent properties. Some chlorinated compounds become good solvents for cellulose esters when mixed with an alcohol. On the other hand, some active solvents for esters of cellulose lose some of their solvent power when mixed with hydrocarbons. Alcohols are added to lacquers to improve flow and to prevent blushing, although they vary considerably in these respects. Al-

TABLE 1.4. DILUTION RATIOS OF VARIOUS MIXTURES[16]

Solvent Mixture	% of Mixture	Toluene	Petroleum Naphtha	Toluene 50% Petroleum Naphtha 50%
Acetone	50			
Butyl alcohol	50	4.60		
Acetone	50			
Ethyl alcohol	50	4.60		
Amyl acetates (mixed isomers)	90			
Amyl alcohols (mixed isomers)	10	2.48		
Amyl acetates (mixed isomers)	85			
Amyl alcohols (mixed isomers)	15	2.46		
Amyl acetates (mixed isomers)	80			
Amyl alcohols (mixed isomers)	20	2.45		
Amyl acetates (mixed isomers)	67			
Amyl alcohols (mixed isomers)	33	2.30		
Amyl acetates (mixed isomers)	55			
Amyl alcohols (mixed isomers)	45	2.00		
Amyl acetates (mixed isomers)	45			
Amyl alcohols (mixed isomers)	55	1.60		
Amyl acetates (mixed isomers)	35			
Amyl alcohols (mixed isomers)	65	1.30		
Amyl acetates (mixed isomers)	30			
Amyl alcohols (mixed isomers)	70	0.90		
Amyl acetates (mixed isomers)	25			
Amyl alcohols (mixed isomers)	75	0.70		
sec-Amyl acetate	67			
sec-Amyl alcohol	33	1.70	1.10	1.30
sec-Amyl acetate	50			
Ethyl acetate	50	2.70	0.75	
n-Butyl acetate	50			
sec-Amyl alcohol	50	2.05	1.00	
sec-Butyl acetate	50			
sec-Amyl alcohol	50	1.90	0.80	
n-Butyl acetate	90			
n-Butyl alcohol	10	3.23		
n-Butyl acetate	80			
n-Butyl alcohol	20	3.20		
n-Butyl acetate	67			
n-Butyl alcohol	33	3.15	1.70	2.15
n-Butyl acetate	60			
n-Butyl alcohol	40	3.10		
n-Butyl acetate	50			
n-Butyl alcohol	50	2.90	1.50	1.90
n-Butyl acetate	40			
n-Butyl alcohol	60	2.50		
n-Butyl acetate	30			
n-Butyl alcohol	70	2.10		
n-Butyl acetate	20			
n-Butyl alcohol	80	1.75		
Butyl acetate	50			
sec-Butyl alcohol	50	2.30	1.00	
sec-Butyl acetate	50			
n-Butyl alcohol	50	2.55	1.20	
sec-Butyl acetate	50			
sec-Butyl alcohol	50	2.20	0.90	
n-Butyl acetate	50			
Ethyl acetate	50	2.85	1.30	2.20

TABLE 1.4. DILUTION RATIOS—*Continued*

Solvent Mixture	% of Mixture	Toluene	Petroleum Naphtha	Toluene 50% Petroleum Naphtha 50%
Butyl acetate	50			
Fusel oil (refined)	50	2.50	1.30	
sec-Butyl acetate	50			
Fusel oil (refined)	50	2.15	1.05	
Diacetone	50			
n-Butyl alcohol	50	3.10		
Diacetone	50			
Ethyl alcohol	50	2.75		
Dibutyl phthalate	50			
n-Butyl alcohol	50	2.70		
Dibutyl phthalate	50			
Ethyl alcohol	50	2.95		
Dibutyl tartrate	50			
n-Butyl alcohol	50	2.70		
Dibutyl tartrate	50			
Ethyl alcohol	50	2.95		
Ethyl acetate	50			
n-Butyl alcohol	50	3.00		
Ethyl acetate	50			
sec-Butyl alcohol	50	2.85	0.75	
Ethyl acetate	50			
Ethyl alcohol	50	3.55		
Ethyl acetate	50			
Fusel oil (refined)	50	2.50	0.95	
Ethyl ether of ethylene glycol	50			
n-Butyl alcohol	50	3.00		
Ethyl ether of ethylene glycol	50			
Ethyl alcohol	50	3.40		
Ethyl ether of ethylene glycol acetate	50			
n-Butyl alcohol	50	2.50		
Ethyl ether of ethylene glycol acetate	50			
Ethyl alcohol	50	3.00		
Ethyl lactate	50			
n-Butyl alcohol	50	3.85		
Ethyl lactate	50			
Ethyl alcohol	50	4.25		
Methyl ethyl ketone	85			
Ethyl alcohol	15	4.97		0.87

cohols are not true or active solvents for nitrocellulose as are the active dissolvents like ethyl lactate or *n*-butyl acetate. The alcohol group, however, cannot be classed as nonsolvents like toluene or naphtha. When an alcohol is added to a true solvent, the solvent power of the latter is not reduced but, on the contrary, this active solvent activates the alcohol to such an extent that it too becomes a solvent. Therefore, alcohols are referred to as *latent solvents*, whose hidden solvent qualities are brought out by the addition of an active solvent. The presence of a latent solvent increases the tolerance of an active solvent for a nonsolvent. This group of latent solvents is also called *extenders*, because they increase the volume of a mixture without decreasing the solvent power.

In general, simple esters and ketones activate alcohols so that they too become solvents and are capable of tolerating various proportions of diluents. This is due to the molecular aggregates formed. Two-type solvents containing both an alcohol and an active solvent group, such as an ester, ether or ketone, activate alcohol to a lesser degree. Unit volumes of a solvent will activate only a limited amount of alcohol, indicating that definite molecular aggregates are formed. A mixture of 50 per cent *n*-butyl acetate and 50 per cent *n*-butyl alcohol will not lose its solvent power until 85 to 95 per cent of the volume is evaporated, contributing further evidence of the validity of the theory of molecular aggregates. Plasticizers, which are the high-boiling solvents, also activate alcohols.

Variation in Evaporation Rate

Liquids vary in their rate of evaporation. Naturally, in a mixture of liquids, some evaporate more rapidly than others. For example, if the solvent constitutent of a lacquer evaporates more rapidly than the diluent, the limit of tolerance of the residual mixture is exceeded and gelling or precipitation occurs. As evaporation goes on, gigantic molecular reactions take place. Vast numbers of molecules change places as the new aggregates are formed. Some are replaced and some are repelled, causing immiscibility, precipitation, blushing, or one or more of the many lacquer faults. It follows that dilution ratios do not indicate tolerance during the change of solvent-nonsolvent balance which occurs during drying. In the theory of molecular aggregation, higher concentrations of cellulose derivatives contain fewer secondary-valence bonds. Consequently, smaller amounts of diluent can be tolerated. This condition occurs during film drying.

Hydroxyl-containing solvents show greater tolerance for toluene than do the simpler esters. In the case of naphtha the condition is reversed. There are, however, exceptions to this statement, among which are butyl lactate and butyl "Cellosolve," which have very high naphtha tolerance. Simple esters will tolerate 50 to 100 per cent more naphtha than will such materials as ethyl lactate, ethyl ether, ethylene glycol, diacetone alcohol, and so forth. Ethers of glycols generally have higher dilution ratios than do the butyl esters with respect to benzene, toluene, and xylene.

Solutions of nitrocellulose tolerate larger quantities of nonsolvents than solutions of cellulose acetate. The "solvent-power number" is influenced by both the nature of the diluent and the mixing of two or more solvents. Frequently, when two or more nonsolvents are mixed, they may exhibit the qualities of a good solvent. This is especially true when one of the ingredients is an alcohol. The ether-alcohol solvent mixture for collodion is an example with which we are most familiar. Another example of acquired solubility is the mixing of butyl acetate with amyl or ethyl alcohol for the less highly polymerized forms of glyceryl phthalate resins. Some of the chlorinated hydrocarbons will dissolve nitrocellulose when mixed with an alcohol. A mixture of benzene and alcohol will dissolve nitrocellulose containing up to 11 per cent nitrogen. A toluene-ethyl alcohol solution of alkyd resin will dissolve nitrocellulose. In many cases the solvent property of esters for resins and nitrocellulose is increased by the addition of an alcohol. On the other hand, when active solvents for cellulose esters are mixed with aliphatic or aromatic hydrocarbons the solvent power of these active solvents is decreased.

These facts bring to light reasons why many of the old-type solvents have been valued for their impurities. For example, methyl acetone, made from the distillation of wood, had particularly valuable solvent properties. Actually, it is a mixed solvent which consists of methanol, acetone, esters and higher ketones. This mixture has certain desirable properties not obtained by any of its component ingredients when used separately. For this reason the "synthetic methyl acetone" is made to simulate it. For this same reason commercial grades of butyl and amyl acetate contain 85 per cent ester and the remaining portion is the corresponding alcohol. Amyl acetate, containing its characteristic impurities when manufactured from fusel oil, is also valued for its solvent properties. The synthetic product is different because it lacks these impurities. It is made from the pentane fraction of gasoline by chlorination; the chloropentane is hydrolyzed to form amyl alcohol, and is finally esterified to the acetate.

According to Reid,[21] alcohols evaporate at a slower rate than their corresponding esters of higher boiling points. This is because there are strong hydroxyl polar groups in the alcohol-containing aggregate. Nonsolvents, owing to the fact that they are so loosely held in aggregate groupings, will leave the film by evaporation, more rapidly than a solvent. Gregg-Wilson and Wright[22] are of the opinion that water dissolves hydroxylic compounds, that benzene dissolves hydrocarbons, and that alcohols have the intermediate position. They further believe that the solubility of complex solutes in solvents is due to the action of different groups in the solvent.

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Chapter 2

Solvents, Latent Solvents, Nonsolvents

Solvent Power and Compatibility

The purpose of solvents is to convert substances into a form suitable for a particular use. The importance of the role of solvents is brought out most clearly by the fact that many substances exhibit their greatest usefulness when in solution. Lacquer solvents, for example, are selected to produce homogeneous combinations and so selected as to impart the most desirable mechanical properties. The physical properties of a fabricated solution can be regulated at will by the proper choice of solvents, thus adapting them to the most varied uses and methods of application. Some of the more important uses for solvents are in lacquers of all kinds, oils, paints, varnishes, polishes, fat extraction and cleaning of metals and fabrics.

The innumerable possible applications of the cellulose derivatives were first revealed in 1868 by John Wesley Hyatt and his classic discovery of celluloid. It required only the recognition of amyl acetate as a desirable nonhygroscopic, medium-boiling solvent to establish the importance of solvents. The modern solvent industry is comparatively new. It was only yesterday, so to speak, that the only industrial solvents were methyl and ethyl alcohols, acetone, glycerol and aliphatic and aromatic hydrocarbons. The rapid growth and wide use of nitrocellulose made new demands upon this industry. In World War I the urgent need for acetone was supplied by the development of a new fermentation process. Butyl alcohol was produced as a by-product, but very little use could be found for it. As the supply increased, activity among research workers was greatly accelerated, with the ultimate employment of butyl esters in flavors, lacquers and plasticizers. The petroleum industry was impelled by the same fever of activity, with the subsequent conversion of ethylene, propylene, butylene and amylene, the olefin fraction of cracked hydrocarbons, to alcohols like ethyl, isopropyl, butyl and amyl. Similarly, the fermentation, coal-tar and synthetic organic chemical industries have long been involved in a competition for supremacy by developing new and improved solvents.

Solvents vary in their dissolving power, so that the line of demarcation between solvents, latent solvents and nonsolvents cannot, with our present knowledge, be clearly defined. Some of the factors which influence solvency are atmospheric conditions, purity and molecular association. Molecular aggregation is the explanation for increased, attenuated, or decreased solvent power or, more concisely, eccentric solvency. Any substance that will dissolve another is called a solvent. Thus, we have a gaseous solution when a liquid or a solid is dissolved in a gas, a liquid solution when any one of these is dissolved in a liquid, and a solid solution when any one of them is dissolved in a solid.

In the opinion of Worden[1] and others, solvents for cellulose ethers and esters owe their solvent action to the presence of the ester, ketone and ether groups. The solubility of these solvents decreases with an increase in molecular weight within a homologous series. In accordance with the theory that like dissolves like, Calvert[2] found that, within certain limits, solvent power increases with increase of the percentage of oxygen within a homologous series of a solvent. This increased solvency is also coupled with a simultaneous decrease in its solubility for unlike materials. In other words, the oxygen contained in a ketone group (R—CO—R) or (—CO—), or in an ester group of organic acids (R—CO—OR), is responsible for their strong solvent action for cellulose esters. Substances having no oxygen in the molecule and those which contain it in the hydroxyl group of higher alcohols are poor or nonsolvents. Cellulose ethers, generally, are soluble in hydrocarbons and cellulose acetate is soluble in chlorinated hydrocarbons.

Some workers are of the opinion that solvent power for nitrocellulose is associated with the —CO— group found in esters, ethers, and ketones. Alcohols, with the exception of methyl and ethyl alcohols, do not dissolve nitrocellulose. These alcohols do not precipitate this cellulose ester as do the nonsolvent hydrocarbons. Sakurado and Kido[3] determined the solvent power of a number of solvents and found them to be as follows: dimethyl acetone, >methyl ethyl acetone, >acetyl ether, >acetyl ethyl ether, >acetyl propyl ether, >pyridine, >acetyl amyl ether, >methyl formate, >acetyl aldehyde, >ethyl carbonate, for nitrocellulose of 13.7 per cent nitrogen, > dimethyl acetone, > methyl ethyl acetone, > pyridine, > acetyl ether, > acetyl ethyl ether, > acetyl amyl ether, >acetyl methyl ether, >methyl formate, >aniline, for 11.6 per cent nitrogen cellulose nitrate.

Nitrocellulose solvents, when measured by their tolerance for diluents, show abnormally high effectiveness, but frequently have little or no solvent power for resins. Conversely, many substances which will not dissolve cellulose esters or ethers, *e.g.*, toluene, xylene, and naphtha, are very good solvents for resins such as ester gum, dammar, and so forth. Many nonsolvent liquids become active solvents when admixed with active or inactive solvent liquid. Examples of this are mixtures of ether-alcohol, alcohol-benzene, alcohol-toluene, and ether-alcohol-butanol. Often such mixtures have constant-boiling properties, which indicate the formation of molecular aggregates. Davidson[4] noted that the solubilities of resins, oils, and gums in glycol ethers increase somewhat with a rise in boiling point.

The solubility also increases with an increase in the oxygen content of the glycol radical.

Lacquer materials are not all compatible with each other. The cellulose esters and ethers and some of the synthetic resins require for their solubility solvents which have one or more ester, ketone, keto-alcohol, hydroxy-ether, or ether groups. On the other hand, gums and resins, such as dammar, kauri and manila, are soluble in hydrocarbons and alcohols. Lacquer solvent combinations should, therefore, contain dissolvent groups for all the ingredients used to make up a lacquer. There are many instances where a combination of certain solvent groups, such as carboxyl, carbonyl and hydroxyl, exerts a dissolving action which is far superior to that of the constituents separately. Some examples of these are the ethyl alcohol-ethyl ether and ethyl alcohol-ethyl acetate combinations.

Likewise, any substance possessing more than one solvent group in its molecule exerts a stronger solvent action than that of a solvent containing only one such group. It is known that the monoethyl ether of ethylene glycol and ethyl lactate, which represent two-type solvents, are powerful dissolving agents. Other binary combinations are ester-alcohol, ether-alcohol, ketone-alcohol, and ester-ether. Diacetone alcohol contains both a ketonic and an alcoholic group, and is a powerful solvent for nitrocellulose and ester gum. In making a solution containing both of these substances, they must be dissolved separately. When these solutions are mixed, a haze results which persists even in the dry film. This fault can be overcome by the addition of a high-boiling solvent like "Hexalin" or ethyl lactate, which contains an ester group and a hydroxyl group. Ethyl lactate is a good solvent for both nitrocellulose and the alcohol-soluble resins like shellac and kauri gum.

When solutions of nitrocellulose and alcohol-soluble gums are each separately dissolved in ethyl lactate and then mixed together, a cloudy solution results. This objectionable haze can be corrected by the addition of butanol. Butyl acetate is another solvent for both nitrocellulose and alcohol-soluble resins. The ether-alcohol odorless solvents comprising methyl, ethyl and butyl ethers of ethylene and diethylene glycol are medium- to high-boiling, and are powerful solvents for nitrocellulose.

According to Doolittle,[5] some of the more commonly used solvents are as follows:* ethyl acetate, butyl acetate, synthetic amyl acetate from pentane, and "Cellosolve" compounds. In the field of low-boilers, ethyl acetate is in a class by itself, as acetone and methyl acetate are much too volatile. Ethyl acetate is also used to blend with butyl and higher acetates. Those solvents used in lesser amounts are isopropyl acetate, secondary butyl and amyl acetates, acetone, methyl ethyl ketone, and ethyl lactate. Mixed esters of secondary and iso-amyl acetates and propionates have been avail-

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*** Arranged in the order of their boiling points.**

able for some years. Esters of lactic acid, such as butyl lactate and others, and the ethers of ethylene glycol, possess the unique property of tolerating large quantities of nonsolvents and diluents.

Catalytic hydrogenation has created high-boiling liquids of strong solvent power, such as cyclohexanol, cyclohexanone, "Tetralin," etc. By high-pressure, catalytic hydrogenation, mineral spirits of paraffinic structure are so altered as to become cyclic bodies with increased solvent power. Naphthas also have been hydrogenated. The higher-boiling ketones are commercial solvents made from the lower ketones; examples of these are methyl isobutyl ketone, methyl amyl ketone and diisobutyl ketone.

Most of the solvents for cellulose acetate are methyl compounds, lower ketones, ketone-alcohols, and cyclic ethers like the dioxanes. A valuable property which many of these compounds possess is water solubility. Although not water-soluble, the chlorinated hydrocarbons possess strong solvent action for cellulose acetate.

Blushing

Gum, cotton, or other types of blush, are caused by precipitation of one or more of the lacquer ingredients during the stages of drying. Rapid evaporation, one causative factor of this precipitation, lowers the temperature; and this results in condensation of water vapor on the surface. This condensed water forms molecular aggregates with some of the ingredients in the lacquer, thus replacing and precipitating gum or a cellulose derivative. Another cause of blush is the evaporation of the active solvent, which leaves the nonvolatile constituents of the lacquer in contact with nonsolvents, with precipitation as the natural consequence. This blush, or precipitation, causes a lack of homogeneity giving, as a result, white or opaque films with inferior strength and durability.

To prevent blushing and to keep the ingredients in solution and uniformly mixed, the solvent blend should be so adjusted as always to contain sufficient active solvent in the residual mixture. The residual solvent mixture must also be of such a nature as to form molecular aggregates with water and still retain its solvent power for the lacquer constituents. In other words, the active solvent mixture must be of such a nature as to tolerate nonsolvents, such as hydrocarbons and water, throughout all the stages of drying. This proper balance of volatile ingredients cannot be too forcibly stressed because of the constant change in ratio between solvent and nonsolvent during the drying period.

Some solvent formulas for experimental dopes have been tried by Reinhart and Kline,[6] and these are given in Table 2.1.

Ware and Bruner[7] have made a very thorough study of the evaluation of nitrocellulose lacquer solvents in relation to three types of diluents, *i.e.*, toluene, gasoline and high-solvency naphtha. These diluents were studied

TABLE 2.1. SOLVENT FORMULAS FOR EXPERIMENTAL DOPES (WEIGHT PER CENT BASIS)[6]

ACETONE	METHYL ETHYL KETONE	ETHYL ACETATE (85–90%)	TOLUENE	*n*-BUTANOL	BUTYL ACETATE	ETHYL LACTATE	DIACETONE ALCOHOL
35	35	..	20	..	..	10	..
35	35	15	..	..	..	15	..
20	..	50	20	..	..	10	..
(70% chloroform and 30% *sym*-tetrachloroethane)							
10	10	..	60 (and 20% "Cellosolve")				
..	..	30	35	5	30	..	..
..	..	32	21	5	42	..	..
30	30	..	30	..	..	..	10
35	..	30	20	..	..	..	15
15	..	25	30	5	25	..	..
..	..	30	35	5	30	..	..
..	..	22	56	5	17	..	..
5	..	20	50	15	10	..	..
30	..	..	60	..	..	..	10
..	10	..	50 (15% methyl acetate and 25% isopropanol)				
..	..	..	74	..	10 (and 16% ethanol)		
..	..	50	25	..	25	..	..
55	20	20	..	..	..	..	5
..	25	25	..	..	25 (and 25% methyl "Cellosolve")		

in conjunction with four commercially available esters: isobutyl acetate (90 per cent), *n*-butyl acetate (90 per cent), isobutyl propionate (80 per cent), and pentacetate (87 per cent). The comparisons were made in the presence of nitrocellulose alone and also with a 2-to-1 mixture of nitrocellulose and resin.

The value as a diluent decreases in the order: toluene, high-solvency naphtha, gasoline; this decrease is considerably greater with nitrocellulose-resin mixtures than when nitrocellulose alone comprises the total solids ingredients; but in no case is it enough to be of any great practical value until a dilution beyond 20 per cent is used.

The complete similarity and equivalence of isobutyl acetate and *n*-butyl acetate is demonstrated as concerns their solvency characteristics and diluent acceptance with the three types of hydrocarbons throughout the entire dilution range at spray viscosity. This equivalence is not noticeably affected by the presence of resin in the formulation. The superior solvent strength of isobutyl propionate as the high-boiling ingredient of nitrocellulose lacquers is shown in Figure 2.4 (page 33).

Germann and Germann[8] have worked out line coordinates representing the solubility curves of a number of substances. They have also compiled some valuable data on the temperature ranges of various solvent mixtures (see Table 2.2).

Mulliken and Wakeman[9] have done some interesting work on hydrocarbon solvent structure as related to miscibility. Their observations and conclusions are repeated here in some detail, as they are deserving of careful consideration.

"The object of this research was to investigate the relation between the structure of hydrocarbons and their miscibility with various organic solvents, in order to use this property as a basis for a qualitative scheme for classifying hydrocarbons experimentally.

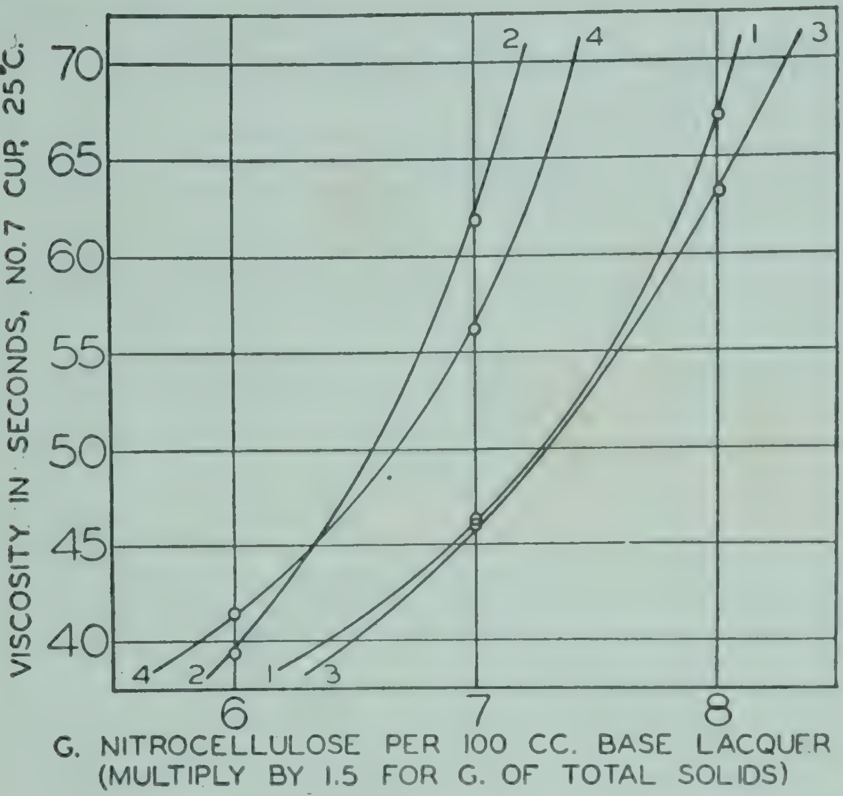

Figure 2.1. Viscosity-Nitrocellulose Content Curves for Isobutyl and *n*-Butyl Acetate at 40:60 Dilution.[7]

1. Isobutyl acetate–toluene
2. Isobutyl acetate–H.S. naphtha
3. *n*-Butyl acetate–toluene
4. *n*-Butyl acetate–H.S. naphtha

"From a study of the literature and a few preliminary experiments, we were led to formulate the following hypotheses:

"1. Those solvents which possess hydroxyl, nitro, or amino groups and which are miscible with aromatic hydrocarbons tend toward immiscibility with the more saturated ones.

"2. The same tendency is shown by neutral sulphates and nitrates of the lower alcohols, but their higher homologs tend toward miscibility with all types of hydrocarbons.

"3. Replacement of hydrogen by alkoxy increases the tendency of a solvent to dissolve hydrocarbons.

"Save for occasional exceptions, the above data show the following general tendencies.

"*Miscibility of Hydrocarbons with Nitromethane.* Among liquid hydrocarbons possessing an equal number of carbon atoms, but different degrees of saturation, the more saturated usually tend to be the less readily miscible with nitromethane. This is especially true in a series where the only structural difference lies in the amount of unsaturation.

"1. Alkanes, cycloalkanes and dicycloalkanes are immiscible with nitromethane at 20° C.

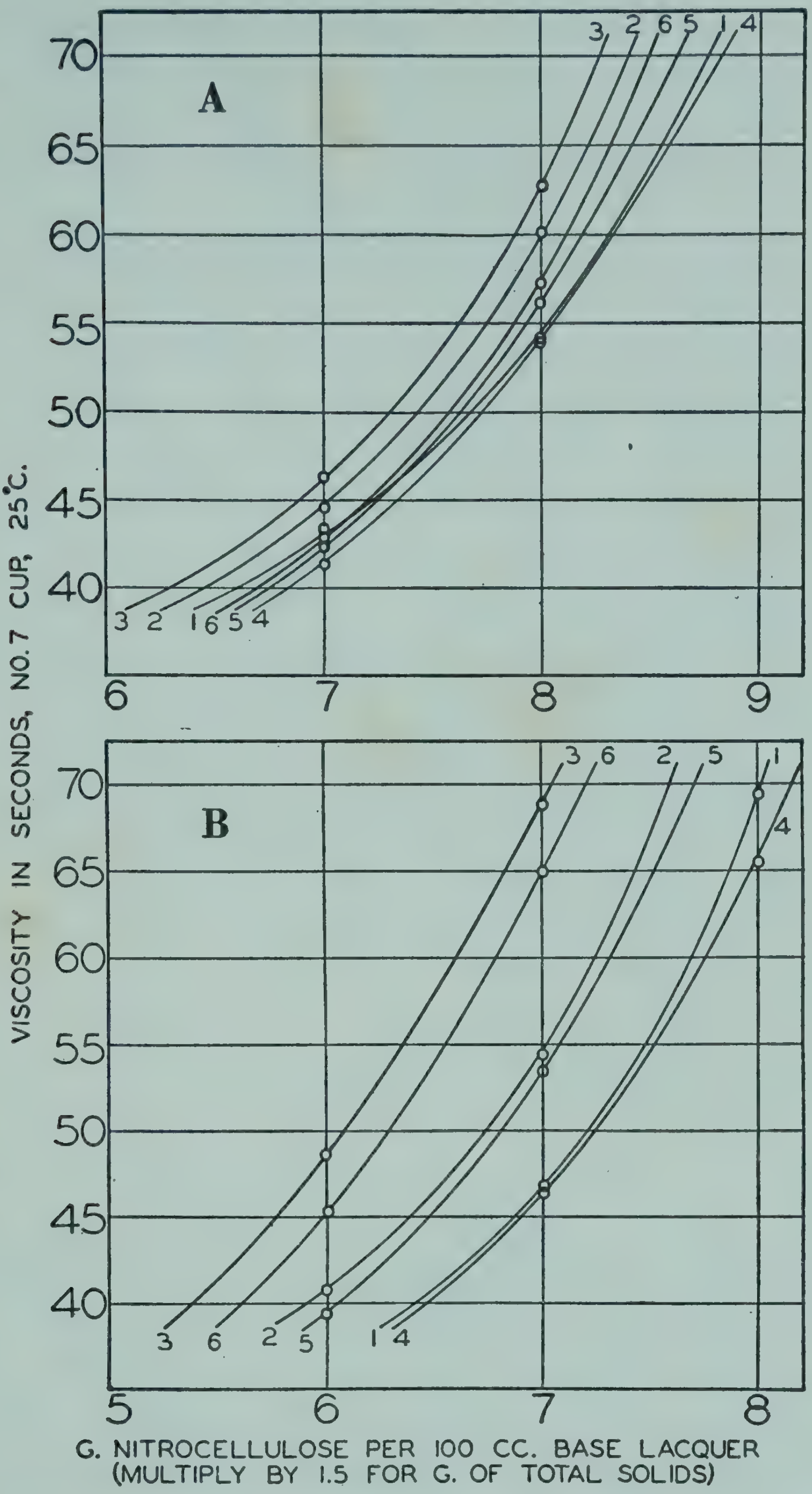

Figure 2.2. Viscosity-Nitrocellulose Content Curves for Isobutyl and *n*-Butyl Acetate at 80:20 (A) and 60:40 (B) Dilutions with a Nitrocellulose:Resin Ratio of 2:1.[7]

1. Isobutyl acetate–toluene
2. Isobutyl acetate–H.S. naphtha
3. Isobutyl acetate–gasoline
4. *n*-Butyl acetate–toluene
5. *n*-Butyl acetate–H.S. naphtha
6. *n*-Butyl acetate–gasoline

"2. Alkenes are usually immiscible with nitromethane at 20° C.

"3. Those cycloalkenes tested are immiscible with nitromethane at 20° C. At C_{10}^{0} presence of an additional double bond or ring system, as in the terpenes, is not sufficient to cause miscibility at 20° C.

"4. Alkadienes containing eight or more carbon atoms are immiscible

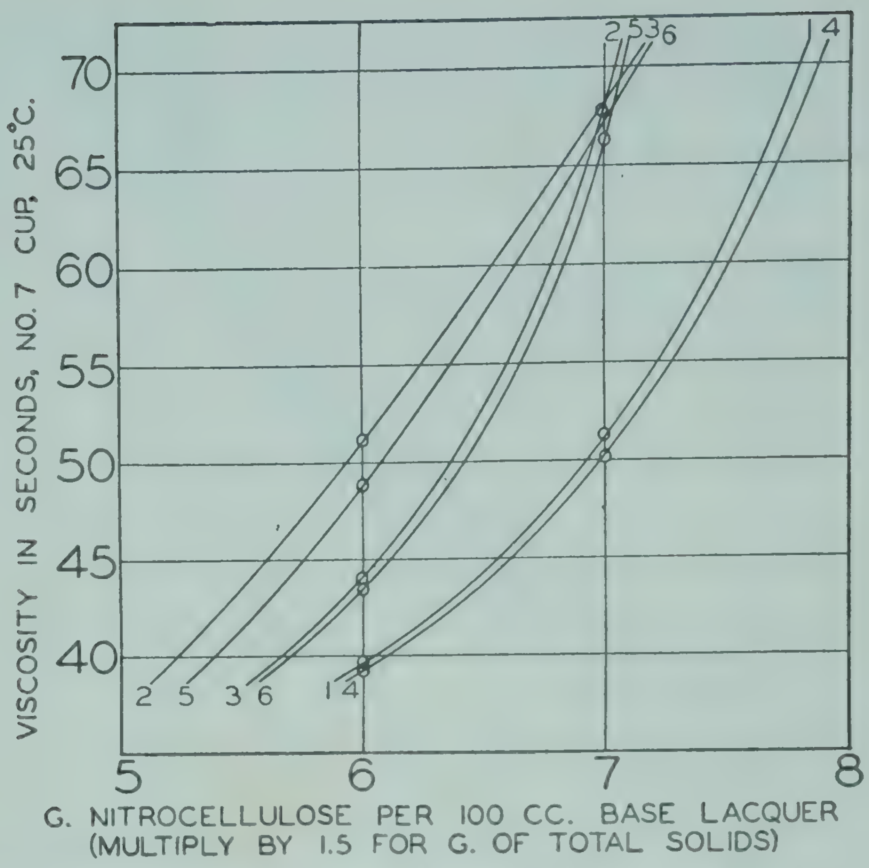

Figure 2.3. Viscosity-Nitrocellulose Content Curves for Isobutyl and *n*-Butyl Acetate at 50:50 and 40:60 Dilution, with a Nitrocellulose:Resin Ratio of 2:1.[7]

1. Isobutyl acetate–toluene (50:50)
2. Isobutyl acetate–H.S. naphtha (50:50)
3. Isobutyl acetate–toluene (40:60)
4. *n*-Butyl acetate–toluene (50:50)
5. *n*-Butyl acetate–H.S. naphtha (50:50)
6. *n*-Butyl acetate–toluene (40:60)

with nitromethane at 20° C; the lower ones are miscible. The tendency of alkadienes, of the same molecular weight, toward miscibility appears to increase as the double bonds approach one another (at least when the final configuration is near the end of the chain).

"5. Alkines whose triple bonds lie near the end of the chain (position 1 or 2) are more soluble in nitromethane than alkadienes of the same molecular weight. Limited data indicate that solubility temperatures rise as the triple bond moves toward the center of the chain.

"6. Aromatics are much more soluble in nitromethane than other types of about the same molecular weight. The lower ones are miscible below 20° C. All of those tested are miscible below 55° C.

"Among the solid hydrocarbons, it appears that, in general, aromatics are much more soluble than nonaromatics of approximately the same molecular weight and melting point.

"*Miscibility of Hydrocarbons with Aniline and Ethyl Sulphate.* The tendency of hydrocarbons of about the same molecular weight to become more readily miscible with increasing unsaturation still holds with these solvents. For a given hydrocarbon, solubility temperatures in them are lower than in nitromethane. Of especial interest is the difference in miscibility of alkenes versus alkadienes and alkines. In general, hydrocarbons of the last two

(*Text continued on page 36*)

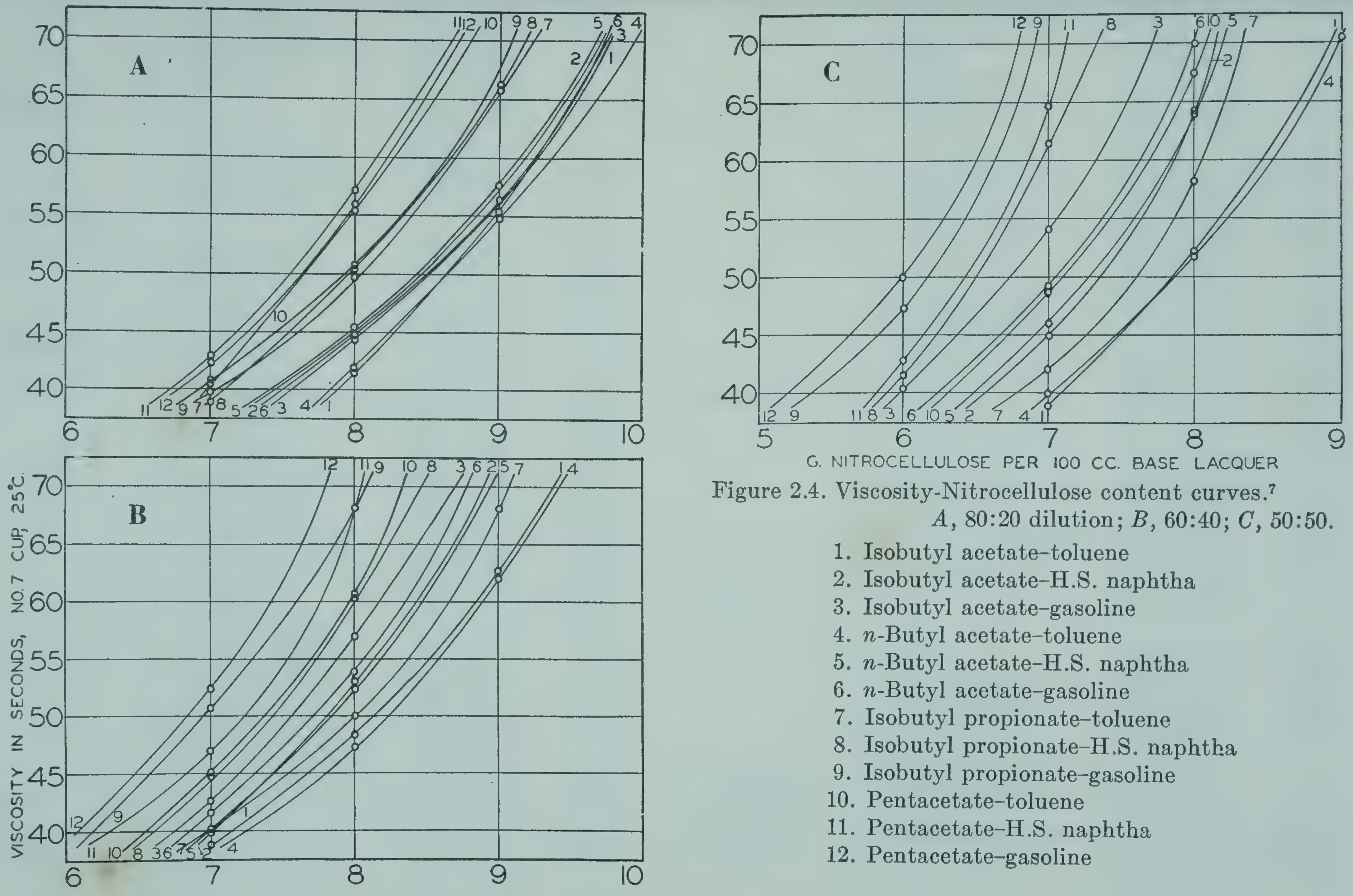

Figure 2.4. Viscosity-Nitrocellulose content curves.[7] *A*, 80:20 dilution; *B*, 60:40; *C*, 50:50.

1. Isobutyl acetate–toluene
2. Isobutyl acetate–H.S. naphtha
3. Isobutyl acetate–gasoline
4. *n*-Butyl acetate–toluene
5. *n*-Butyl acetate–H.S. naphtha
6. *n*-Butyl acetate–gasoline
7. Isobutyl propionate–toluene
8. Isobutyl propionate–H.S. naphtha
9. Isobutyl propionate–gasoline
10. Pentacetate–toluene
11. Pentacetate–H.S. naphtha
12. Pentacetate–gasoline

TABLE 2.2[8]

Solute (Solid Phase)	Solvent (Liquid Phase)	Temp. Range, ° C.	Eutectic Temp., ° C.
Benzene	1. Phenol	−4.0 to 5.5	−5.3
	2. Nitrobenzene	−24.6 to 5.5	−24.6
	3. *o*-Bromonitrobenzene	−8.7 to 5.5	−8.7
	m-Bromonitrobenzene	−3.1 to 5.5	−3.1
	p-Bromonitrobenzene	3.7 to 5.5	3.7
	Diphenylamine	−6.8 to 5.5	−6.8
	4. Benzoyl chloride	−20.0 to 5.5	−26.5
	m-Dinitrobenzene	−0.8 to 5.2	−0.8
	2,4-Dinitrotoluene	−0.7 to 5.2	−0.7
	2,6-Dinitrotoluene	0.2 to 5.2	0.2
	3,4-Dinitrotoluene	−5.0 to 5.2	−5.0
	5. Nitrobenzyl chloride	−3.3 to 5.5	−3.3
	Pyridine	−40.0 to 5.5	−41.0
	6. Bromoform	−15.0 to 5.5	−26.0
	o-Chloronitrobenzene	−10.6 to 5.5	−10.6
	m-Chloronitrobenzene	−5.7 to 5.5	−5.7
	p-Chloronitrobenzene	−4.0 to 5.5	−4.0
	7. *p*-Bromotoluene	−18.5 to 5.48	−18.5
	Diphenyl	−5.8 to 5.48	−5.8
	Ethylene dibromide	−27.6 to 5.5	−27.6
	8. Ethylene dichloride	−53.0 to 5.5	−53.0
	Naphthalene	−3.5 to 5.5	−3.5
	Paraldehyde	−27.0 to 5.5	−27.0
	Toluene	−70.0 to 5.5	−99.8
	p-Xylene	−22.2 to 5.5	−22.2
	9. Camphene	−20.0 to 5.5	−45.0
Ethylene dibromide	1. Paraldehyde	−10.0 to 9.7	−20.0
	2. Toluene	−40.0 to 9.7	...
	3. *p*-Xylene	−20.0 to 9.7	−20.0
	4. Benzene	−20.0 to 9.7	−27.6
	Diphenylamine	−5.3 to 9.7	−5.3
	Naphthalene	0.25 to 9.7	0.25
	5. *p*-Bromotoluene	−10.0 to 9.7	−12.4
Acetic acid	1. Dimethyl oxalate	8.4 to 16.7	8.4
	2. Benzoic acid	9.5 to 16.7	9.5
	Dimethyl succinate	−7.0 to 16.7	−7.0
	3. Phenol	−15.0 to 16.7	−15.0
	4. α-Chloroacetic acid	−4.0 to 16.7	−4.0
Phenol	1. Benzene	20.0 to 40.6	−5.3
	2. Acetic acid	10.0 to 40.5	−15.0
	3. Nitrobenzene	5.0 to 40.5	−16.5
	4. α-Chloroacetic acid	25.0 to 42.4	16.5
	β-Chloroacetic acid	25.0 to 42.4	11.8
	5. *m*-Hydroxybenzaldehyde	22.0 to 41.0	22.0
Naphthalene (*Continued*)	14. Diphenyl	39.4 to 80.09	39.4
	Ethylene dibromide	30.0 to 80.1	0.25
	15. Chlorobenzene	−10.0 to 80.1	...
	Ethylene dichloride	−10.0 to 80.1	...
	Pyridine	0.0 to 80.1	−41.0
	16. Chloroform	10.0 to 80.1	...
	Diphenylamine	40.0 to 80.1	30.5
	Diphenylmethane	14.5 to 80.1	14.5
	p-Nitrotoluene	40.0 to 80.1	29.0
	17. Fluorene	55.0 to 80.1	55.0
	18. Camphor	32.3 to 80.1	32.3
***p*-Dibromobenzene**	1. Aniline	20.0 to 89.0	...
	2. Nitrobenzene	20.0 to 89.0	...
	3. Ethyl ether	10.0 to 87.0	...
	4. Carbon tetrachloride	20.0 to 89.0	...
	m-Chloronitrobenzene	34.0 to 88.3	34.0
	5. Benzene	10.0 to 87.0	...
	Carbon disulfide	0.0 to 87.0	...
	Toluene	10.0 to 89.0	...
	6. Bromobenzene	5.0 to 87.0	...
	7. *o*-Dibromobenzene	20.0 to 86.7	0.3
Acenaphthene	1. Acetone	10.0 to 95.0	...
	2. Aniline	10.0 to 95.0	...
	3. Carbon tetrachloride	10.0 to 95.0	...
	4. Pyridine	20.0 to 95.0	...
	5 Carbon disulfide	10.0 to 95.0	...
	o-Dinitrobenzene	71.5 to 92.5	71.5
	6. Nitrobenzene	10.0 to 95.0	...
	Toluene	10.0 to 95.0	...
	7. Indene	30.0 to 95.0	...
	8. Chlorobenzene	10.0 to 95.0	...
	p-Dinitrobenzene	81.5 to 92.5	81.5
	9. Fluorene	67.5 to 95.0	67.5
	10. Chloroform	50.0 to 95.0	...
	11. Iodoacenaphthene	50.0 to 92.5	37.6
	12. Chloroacenaphthene	56.6 to 92.5	56.6.
Phenanthrene	1. Acetone	−10.0 to 30.0	...
	2 Benzene	5.0 to 75.0	...
	3. Toluene	0.0 to 90.0	...
	4. Chlorobenzene	10.0 to 80.0	...
	5. Pyridine	5.0 to 75.0	...
	6. Nitrobenzene	5.0 to 85.0	...
	7. Chloroform	−10.0 to 30.0	...
	8. Tetrachloroethane	0.0 to 85.0	...

o-Nitrophenol	1.	Naphthalene	29.0 to 45.0	29.0
	2.	p-Nitrophenol	33.5 to 44.0	33.5
	3.	m-Nitrophenol	31.5 to 44.0	31.5
	4.	β-Naphthylamine	36.3 to 44.5	36.3
	5.	α-Naphthylamine	20.0 to 44.5	14.0
	6.	Picric acid	34.0 to 45.5	34.0
		p-Toluidine	15.0 to 44.5	15.0
p-Nitrotoluene	1.	Naphthalene	35.0 to 52.0	29.0
	2.	2,4-Dinitrotoluene	26.5 to 51.4	26.5
		2,6-Dinitrotoluene	30.0 to 51.4	...
	3.	m-Dinitrobenzene	29.7 to 51.4	29.7
		o-Nitrotoluene	15.0 to 51.4	−16.3
		m-Nitrotoluene	15.0 to 51.4	−2.8
α-Chloroacetic acid	1.	o-Cresol	15.8 to 61.7	15.8
		m-Cresol	5.0 to 61.7	...
		p-Cresol	20.0 to 61.7	13.4
	2.	Salol	26.7 to 61.4	26.7
	3.	Benzoic acid	46.7 to 61.7	46.7
		Phenol	16.5 to 61.7	16.5
	4.	o-Toluic acid	47.3 to 61.7	47.3
	5.	m-Toluic acid	46.5 to 61.7	46.5
		p-Toluic acid	56.8 to 61.7	56.8
	6.	Cinnamic acid	47.6 to 61.7	47.6
	7.	Crotonic acid	26.0 to 61.7	26.0
	8.	Phenylacetic acid	30.5 to 61.7	30.5
	9.	Acetic acid	−4.0 to 61.7	−4.0
2,4-Dinitrotoluene	1.	Benzene	−0.7 to 70.7	...
	2.	o-Dinitrobenzene	55.4 to 69.5	55.4
		m-Dinitrobenzene	44.9 to 69.5	44.9
		Fluorene	55.0 to 69.0	...
	3.	Picric acid	53.3 to 69.5	53.3
	4.	2,6-Dinitrotoluene	33.6 to 70.1	33.6
	5.	o-Nitrotoluene	15.0 to 70.1	−11.45
		p-Nitrotoluene	30.0 to 70.1	26.5
Naphthalene	1.	Benzoic acid	70.0 to 80.1	70.0
	2.	Hexane	10.0 to 80.1	...
	3.	α-Naphthol	61.0 to 80.0	61.0
	4.	p-Toluidine	40.0 to 80.1	31.9
	5.	Acetone	10.0 to 80.1	...
	6.	Ethyl ether	15.0 to 35.0	...
	7.	Ethyl acetate	10.0 to 80.1	...
	8.	Camphene	7.5 to 80.1	7.5
	9.	Carbon tetrachloride	0.0 to 80.1	...
	10.	o-Dinitrobenzene	62.0 to 80.1	62.0
	11.	Toluene	20.0 to 80.0	...
		Indene	30.0 to 80.1	...
	12.	Nitrobenzene	20.0 to 80.1	−3.0
		Benzene	−3.5 to 80.1	−3.5
		Phthalic anhydride	64.9 to 80.05	64.9
	13.	α-Nitronaphthalene	60.0 to 80.0	36.7
		o-Nitrophenol	29.0 to 80.1	29.0
Fluorene	1.	Acetone	10.0 to 50.0	...
	2.	Aniline	10.0 to 114.5	...
	3.	Carbon tetrachloride	10.0 to 60.0	...
	4.	Pyridine	10.0 to 114.5	...
	5.	Benzene	10.0 to 114.5	...
		Toluene	10.0 to 114.5	...
		Xylene	10.0 to 114.5	...
	6.	Nitrobenzene	10.0 to 114.5	...
	7.	Chlorobenzene	40.0 to 114.5	...
		Indene	10.0 to 114.5	...
	8.	o-Dinitrobenzene	78.0 to 112.5	...
	9.	Acenaphthene	65.7 to 113.5	65.7
	10.	Naphthalene	55.0 to 114.5	55.0
	11.	2,4-Dinitrophenol	74.0 to 112.5	74.0
	12.	m-Dinitrobenzene	70.0 to 112.5	54.0
		p-Dinitrobenzene	95.0 to 112.5	90.0
Benzoic acid	1.	m-Hydroxybenzaldehyde	95.0 to 121.5	83.0
	2.	Carbon tetrachloride	10.0 to 40.0	...
	3.	Naphthalene	70.0 to 121.0	70.0
	4.	Nitrobenzene	10.0 to 80.0	...
	5.	Benzil	95.0 to 121.4	77.2
	6.	Piperonal	50.0 to 121.4	27.3
	7.	Acetic acid	40.0 to 121.4	9.5
	8.	Acetophenon	10.0 to 121.4	...
	9.	α-Chloroacetic acid	60.0 to 121.5	46.7
	10.	o-Chlorobenzoic acid	91.2 to 121.7	91.2
		m-Chlorobenzoic acid	95.4 to 121.7	95.4
		p-Chlorobenzoic acid	115.0 to 121.7	115.0
	11.	Cinnamic acid	82.0 to 121.5	82.0
Camphor	1.	Naphthalene	100.0 to 197.0	32.3
	2.	β-Naphthylamine	80.0 to 179.0	55.0
		α-Nitronaphthalene	27.3 to 179.0	27.3
Anthracene	1.	p-Nitrophenol	150.0 to 212.5	106.0
	2.	Chrysene	193.5 to 216.5	193.5
	3.	β-Naphthol	110.0 to 213.0	110.0
	4.	β-Naphthylamine	98.0 to 213.0	98.0
	5.	Nitrobenzene	5.0 to 175.0	...
	6.	p-Dinitrobenzene	146.0 to 212.5	146.0
	7.	2,4-Dinitrophenol	101.0 to 213.0	101.0
Carbazole	1.	Pyrogallol	126.0 to 236.0	126.0
	2.	Resorcinol	160.0 to 236.0	...
	3.	Catechol	102.0 to 236.0	102.0
	4.	p-Nitrophenol	106.7 to 236.0	106.7
	5.	β-Naphthol	135.0 to 235.5	115.0
	6.	m-Nitrophenol	92.0 to 236.1	92.0
	7.	α-Naphthol	90.0 to 235.6	90.0
	8.	o-Nitrophenol	43.5 to 236.0	43.5

classes have lower solubility temperatures than alkenes of the same molecular weight.

"*Miscibility of Hydrocarbons with Benzyl Alcohol.* In general, alkanes are immiscible with benzyl alcohol at temperatures at which cycloalkanes of the same molecular weight are miscible. In the cases tested, alkanes were immiscible at 50° C, cycloalkanes miscible.

"*Classification of Hydrocarbons of Unknown Structure.* From the foregoing, it will be seen that if a hydrocarbon of unknown structure is not acetylenic, its miscibility with nitromethane (at 20° C. for b.p. 110–220° C. or at 55° C. for b.p. 220–300° C) will usually indicate whether or not it is aromatic, aromatics being miscible.

"If an unsaturated nonaromatic hydrocarbon is known to be acyclic, the presence of a single double bond, or of a higher degree of unsaturation can usually be shown by its miscibility with aniline, the temperature of the test depending upon the boiling point, alkenes being immiscible.

"Finally, whether a saturated nonaromatic hydrocarbon is cyclic or acyclic can usually be determined by testing its miscibility with benzyl alcohol at 50° C., for example, cyclics being miscible."

Classification of Solvents

Owing to the wide differences in physical and chemical properties of solvents and their use in a large variety of products, it is difficult to classify them in order to meet the demands of all. Some advocate a grouping according to evaporation rates while others think dilution ratios are more useful. Like all methods of classification these have their advantages and disadvantages. None gives a complete picture comprising purity, density, stability, evaporation rates, dilution ratios and so forth. The following is a classification according to boiling points:

By Boiling Point

Low Boilers

Those which boil below 100° C. usually have fast evaporation rates, and dry quickly; many reduce viscosity, many have pleasant odors. These are generally the active solvents or diluents.

Acetone
Acetylene dichloride
Benzene
sec-Butyl alcohol
Butyl chloride
Carbon disulfide
Carbon tetrachloride
Cyclohexane
Diethyl carbonate
Diethyl ketone
Ethyl acetate
Ethyl alcohol
Ethyl bromide
Ethyl ether
Ethyl propionate
Ethylene dichloride
Ethylene trichloride
Ethylidene chloride

Isoamyl chloride
Isobutyl formate
Isopropyl acetate
Isopropyl alcohol
Methyl acetate
Methyl acetone
Methyl alcohol
Methyl carbonate
Methyl ether
Methyl ethyl ketone
Methyl formate
Methyl propionate
Methyl propyl ketone
Methylene chloride
Petroleum naphtha
Propyl alcohol
Propyl ether
Propyl formate
Propylene dichloride
"Solvesso" No. 1*

Medium Boilers

Those which have boiling points ranging between 100 and 150° C. and usually impart the properties of flow to a lacquer.

n-Amyl acetate
Amyl acetate (mixed isomers)
sec-Amyl acetate
n-Amyl alcohol
Amyl alcohol (mixed isomers)
sec-Amyl alcohol
n-Butyl acetate
sec-Butyl acetate
n-Butyl alcohol
sec-Butyl alcohol
n-Butyl propionate
"Cellosolve"
"Cellosolve" acetate
Cyclohexanone
Diethyl carbonate
Diethyl "Cellosolve"
Dipropyl ketone
Furfural
sec-Hexyl acetate
Hi-Flash naphtha
Isobutyl acetate
Isobutyl alcohol
Isopropyl "Cellosolve"
Isopropyl lactate
Mesityl oxide
3-Methoxy butyl acetate
Methyl amyl acetate
Methyl amyl alcohol
Methyl *n*-amyl ketone
Methyl *n*-butyl ketone
Methyl "Cellosolve"
Methyl "Cellosolve" acetate
Methyl cyclohexanone
Methyl isobutyl ketone
Methyl propyl ketone
Monochlorobenzene
"Solvesso" Nos. 1 and 2
Tetrahydrofurfuryl alcohol
Toluene
V. M. & P. Naphtha
Xylene

High Boilers

Those which boil between 150 and 200° C. These are the residual solvents with low evaporation rates and strong solvent power. They prevent blush or precipitation and impart final flow, resulting in smooth and glossy films.

Acetonyl acetone
Benzyl alcohol
Benzyl "Cellosolve"
Butyl butyrate
Butyl "Carbitol"
Butyl "Carbitol" acetate
Butryl "Cellosolve"
Butyl "Cellosolve" acetate

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* For the chemical name of this and other trade mark products see under their separate treatment in later chapters.

Butyl lactate
"Carbitol"
"Carbitol" acetate
Cyclohexanol
Cyclohexanyl acetate
Decahydronaphthalene ("Decalin")
Diacetone alcohol
Dichloroethyl ether
Diethyl "Carbitol"
Diethyl oxalate
Diglycol diacetate
Diisobutyl ketone
Ethyl acetoacetate
Ethyl benzoate
2-ethylbutyl acetate
2-ethyl hexyl alcohol
Ethyl lactate
Fenchone
Furfuryl acetate
Furfuryl alcohol
Glycol diacetate
"Hercosol"
Isophorone
Methyl "Carbitol"
Methyl "Carbitol" acetate
Methyl *n*-hexyl ketone
Orthodichlorobenzene
Pine oil (heavy)
"Safe-T-Esso"
"Solvesso" No. 3
Turpentine (gum spirits)
Turpentine (steam distilled)
V. M. & P. naphtha (long cut)

Plasticizers and Softeners

These solvents have boiling points of 300° C. or over and constitute a permanent part of the film. They impart toughness and flexibility.

By Chemical Structure

Aliphatic Hydrocarbons

Gasoline
Hi-Flash naphtha
Mineral spirits
Petroleum benzene
Petroleum naphtha
V. M. & P. naphtha

Aromatic Hydrocarbons

Benzene
Decahydronaphthalene ("Decalin")
1-Methyl-4-isopropyl benzene
p-Cymene
Tetrahydronaphthalene ("Tetralin")
Toluene
Xylene

Halogenated Aliphatic and Aromatic Hydrocarbons

Dichloroethylene
Dichloroethyl ether
Ethylene dichloride
Methylene chloride
Monochlorobenzene
o-Dichlorobenzene
Tetrachloroethylene
Trichloroethylene

Alcohols

Amyl alcohol
Benzyl alcohol
Butyl alcohol
Cyclohexanol
Ethyl alcohol
2-Ethyl butyl alcohol
2-Ethyl hexyl alcohol
Isopropyl alcohol
Methyl alcohol
Methyl amyl alcohol

Ketones

Acetone
Acetonylacetone
Cyclohexanone
Diacetone alcohol
Diisobutyl ketone
Diethyl ketone
Dipropyl ketone
Isophorone
Mesityl oxide
Methyl acetone*
Methyl amyl ketone
Methyl butyl ketone
Methyl cyclohexanone
Methyl dipropyl ketone
Methyl ethyl ketone
Methyl *n*-hexyl ketone
Methyl isobutyl ketone
Methyl propyl ketone

Esters

Acetates
Alkyl formates
Lactates
Propionates

Ethers

Butyl ether
Diethyl "Carbitol"
Diethyl "Cellosolve"
Ethyl ether
Isopropyl ether

Alcohol Esters

Butyl lactate
Diethyl malate
Diethyl tartrate
Ethyl glycollate
Ethyl hydroxypropionate
Ethyl lactate
Isopropyl lactate
Triethyl citrate

Ether-Alcohols

Benzyl "Cellosolve"
Butyl "Carbitol"
Butyl "Cellosolve"
"Carbitol"
"Cellosolve" glycol ethers
Diethyl glycerol ether
Glycidol
Isopropyl "Cellosolve"
Methyl "Carbitol"
Methyl "Cellosolve"
Monoethyl ether of triethylene glycol

Ketone-Alcohols

Acetonyl methanol
Diacetone alcohol
Dihydroxyl acetone
Pyruvyl alcohol

Ketone-Esters

Ethyl acetoacetate
Ethyl pyruvate

Ketone-Ethers

Acetal ethyl ether (ethoxy acetone)
Ethyl ether of acetonyl methanol
Methyl ethoxy ethyl ether

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* Methyl acetone is a commercial mixture of acetone 48 per cent, methyl acetate 28 per cent, methanol 24 per cent.

TABLE 2. 3. Miscibilities of Liquid Alkanes and Cycloalkanes with Certain Selective Solvents[9]

HYDROCARBON	B.P. (°C)	WITH NITROMETHANE		WITH ANILINE		WITH ETHYL SULPHATE		WITH BENZYL ALCOHOL	
		Temp. of Test* (°C)	Sol. Temp. (°C)	Temp. of Test* (°C)	Sol. Temp. (°C)	Temp. of Test* (°C)	Sol. Temp. (°C)	Temp. of Test* (°C)	Sol. Temp. (°C)
Alkanes									
Hexane	69–70	i 95	106	i 60	65	i 60	69	i 50	57
Heptane	ca 98	i 20	—	—	—	—	—	i 20	—
2,2,4-Tri-methylpentane	98–99	i 105	—	i 70	78	i 65	73	i 60	74
Octane	ca 125	i 20	—	i 60	67	70	79	i 40	55
Nonane	ca 150	i 85	—	—	—	—	—	—	—
2,7-Di-methyloctane	159–60	i 30	—	i 70	77	80	90	i 60	72
Decane	ca 173	i 30	—	i 35	—	—	—	i 50	—
Tetradecane	ca 252	i 30	—	i 60	—	—	—	i 70	—
Cycloalkanes									
Cyclohexane	ca 80	i 20	—	i 20	—	i 20	—	m 20	—
Methylcyclohexane	ca 101	i 20	—	i 20	—	—	—	m 30	—
Dimethylcyclohexane	ca 120	i 95	107	—	—	—	—	—	—
p-Menthane	ca 169	i 20	—	i 35	—	—	—	m 50	—
Decahydronaphthalene	ca 190	i 50	—	i 20	—	i 30	—	m 20	—
Ter-amyl-cyclohexane	191–192	i 65	73	—	—	—	—	—	—

Miscibilities of Other Liquid Non-aromatic Hydrocarbons with Certain Selective Solvents

HYDROCARBON	B.P. (°C)	WITH NITROMETHANE		WITH ANILINE		WITH ETHYL SULPHATE	
		Temp. of Test* (°C)	Sol. Temp. (°C)	Temp. of Test* (°C)	Sol. Temp. (°C)	Temp. of Test* (°C)	Sol. Temp. (°C)
Alkenes							
Pentene-(1)	30.4–30.6	i 40	—	—	—	—	—
Amylene	ca 36	i 10	18	m 20	—	m 20	—
Pentene-(2)†	36.4–36.5	i 40	—	—	—	—	—
4-Methyl-pentene-(1)	55.0–55.5	i 25	—	i 20	—	—	—
2,3-Dimethyl-butene-(1)†	58–59	i 60	—	i 20	25	—	—
4-Methyl-pentene-(2)	58.6–59.0	i 75	—	i 20	41	i 15	22
Hexene-(1)	63.6–64.1	i 70	—	i 20	—	m 20	—
Hexene-(2)†	68.0–68.2	i 25	65	—	—	—	—
2,3-Dimethyl-butene-(2)†	71.5–72.0	i 25	51	i 10	12	—	—
2,4-Dimethyl-pentene-(2)	82.9–83.4	i 25	65	i 20	—	—	—
5-Methyl-hexene-(1)	85.5–86.0	i 25	—	i 20	32	i 10	16
4-Methyl-hexene-(1)	86.8–87.3	i 25	—	i 25	—	m 20	—
Heptene-(1)	94.0–94.4	i 70	—	i 20	—	m 20	—
Heptene-(3)	95.8–96.3	i 25	65	i 20	39	—	—
Heptene-(2)	98.6–99.6	i 25	67	i 20	28	i 10	14
Diisobutylene	ca 102	i 25	—	i 25	—	i 25	—
4-Methyl-heptene-(2)	113.8–14.1	i 25	81	i 20	42	i 20	37
Octene-(2)	ca 125	i 25	—	i 30	33	i 10	12

TABLE 2. 3. *Continued*

MISCIBILITIES OF OTHER LIQUID NON-AROMATIC HYDROCARBONS WITH CERTAIN SELECTIVE SOLVENTS

HYDROCARBON (*Alkenes*)	B.P. (°C)	WITH NITROMETHANE		WITH ANILINE		WITH ETHYL SULPHATE	
		Temp. of Test* (°C)	Sol. Temp. (°C)	Temp. of Test* (°C)	Sol. Temp. (°C)	Temp. of Test* (°C)	Sol. Temp. (°C)
4,5,5-Trimethyl-hexene-(2)	128.7–29.5	i 25	88	i 30	52	i 20	41
4,6-Dimethyl-heptene-(2)	129.5–30.1	i 25	98	i 30	55	i 20	48
4,5-Dimethyl-heptene-(2)	135.0–36.1	i 100	—	i 30	52	i 20	46
4-Methyl-octene-(2)	137.3–37.9	i 25	101	i 30	50	i 20	48
Nonene-(1)	145.3–45.8	i 25	84	i 30	40	i 20	38
Nonene-(4)	147.5–48.1	i 25	84	i 30	45	—	—
Decene-(1)	170.4–70.8	i 100	—	i 30	48	i 40	—
Triisobutylene	ca 177	i 110	—	—	—	—	—

MISCIBILITIES OF SOLID HYDROCARBONS WITH NITROMETHANE

HYDROCARBON	B.P. (°C)	M.P. (°C)	WITH NITROMETHANE	
			Temp. of test* (°C)	Sol. temp. (°C)
Non-aromatic				
Camphene	ca 160	ca 50	i 50	77
Dicyclopentadiene	ca 170	ca 32	i 50	60
Cetene	181.4–83.6 at 43 mm	4–5	i 120	—
Hexadecine-(1)	156–57/15 mm	17	i 80	92
Aromatic				
Benzene	ca 80	ca 5	m −10	—
Durene	ca 191	ca 77	m 100	—
Naphthalene	ca 218	ca 80	m 45	—
Phenylcyclohexane	ca 238	ca 7	m 40	24
β-Methylnaphthalene	ca 240	ca 32	m −10	—
Diphenyl	ca 255	ca 69	m 30	—
2,6-Dimethylnaphthalene	ca 261	ca 110	m 80	62
Diphenylmethane	ca 261	ca 26	m −10	—
Hexamethylbenzene	ca 265	ca 160	m 100	—
Dihenzyl	ca 284	ca 50	m 50	—
Octabydroanthracene	ca 292	ca 71	m 85	76
p,p′-Ditolyl	ca 295	ca 121	m 80	69
Hexaethylbenzene	ca 298	ca 128	m 83	—
1,1,2-Triphenylethylene	ca 220/14 mm	ca 67	m 35	21
Anthracene	ca 351	ca 216	m 100	—
9-Isoamylanthracene	—	58–59	m 20	—
Tetraphenylethylene	ca 415	ca 223	m 100	—

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* m = miscible; i = immiscible.

† From Dr. H. E. Buc, Standard Oil Development Co., Elizabeth, N. J.

Ester-Ethers

Butyl "Carbitol" acetate
Butyl "Cellosolve" acetate
"Carbitol" acetate
"Cellosolve" acetate
Diglycol diacetate
3-Methoxy butyl acetate
Methyl "Carbitol" acetate
Methyl "Cellosolve" acetate

Ether-Alcohol-Ester

Diethylene glycol monoacetate

Requirements of Solvents

1. Lacquer solvents should possess active solvent properties for cellulose esters and ethers, gums and resins, and should be able to dissolve these substances in any desired proportion.

2. They should possess the property of wetting pigments.

3. Rate of evaporation should be uniform, or nearly so, to produce maximum gloss and finish.

4. They should be colorless or nearly so.

5. They should be odorless or nearly so (nothing persistent).

6. They should be neutral in reaction.

7. They should be stable to chemicals, water, atmospheric conditions and aging, and should not break down in structure.

8. They should tolerate large amounts of nonsolvents without blushing or precipitation.

9. They should be nontoxic to insure the health of users.

10. They should be free from water.

11. Boiling point or range should indicate purity.

12. The evaporation rate should not produce too great a drop in temperature.

13. They should have minimum lifting action on varnish and paint films.

14. Good blending properties are essential.

15. The cost should be moderate, and the solvent should be commercially abundant, and have a low specific gravity.

Requirements of Mixed Solvents

1. They should hold the nonvolative ingredients until the film has dried.

2. The active solvent should evaporate at a slower rate than the nonsolvent and thus prevent blush or precipitation.

3. The active solvent should be the last to leave the film, but prior to this it should produce a flow resulting in a smooth glossy surface free from gas bubbles.

4. These mixtures should produce uniform blending of all the lacquer ingredients during the stages of drying.

5. When employed as thinners, they must cut the lacquer base readily.

TABLE 2.4. Solubility of Water in Solvents (by Weight in 100 Parts Solvent at 20° C)

Acetoacetanilide	S.S.
Acetone	M
Acetonylacetone	M
Acetylene tetrachloride	insol.
Amyl acetate (mixed isomers)	1.15
sec-Amyl acetate	0.9
Amyl alcohol (mixed isomers)	9.0
sec-Amyl alcohol	9.9
Benzene	insol.
Benzyl alcohol	8.4
Benzyl ether of ethylene glycol	18.1
n-Butyl acetate	1.86
sec-Butyl acetate	1.65
Butyl acetyl ricinoleate	2.1 (25° C)
n-Butyl alcohol	19.50
sec-Butyl alcohol	44.1 (25°C)
Butyl butyrate	0.43
Butyl ether	insol.
Butyl ether of diethylene glycol	M
Butyl ether of diethylene glycol acetate	3.4
Butyl ether of ethylene glycol	M
Butyl ether of ethylene glycol acetate	1.9
Butyl lactate	14.5
n-Butyl propionate	0.8
Butyl stearate	0.04 (25° C)
Chloroform	insol.
Cyclohexane	insol.
Cyclohexanol	11.8
Cyclohexanone	8.7
Cyclohexanyl acetate	1.4
Decahydronaphthalene	insol.
Diacetin	M
Diacetone alcohol	M
Dibutyl phthalate	0.3 (25° C)
Dichlorethyl ether	0.1
Dichlorodiethyl ether	insol.
Diethanolamine	M
Diethyl carbonate	2.6
Diethyl ether of ethylene glycol	4.5
Diethyl ether of ethylene glycol acetate	M
Diethyl ketone	2.1
Diethyl sulfate	0.7
Diethylene glycol	M
Diglycol diacetate	M
Diisobutyl ketone	S.S.
Dimethyl ether of ethylene glycol	M
Dimethyl phthalate	2.2
1,4-Dioxane	M
Dipentene	insol.
Dipropyl ketone	0.9
Ethyl acetate	11.0
Ethyl acetoacetate	2.8
Ethyl alcohol (anhydrous)	M
Ethyl alphahydroxyisobutyrate	M
2-Ethyl butyl acetate	0.6
2-Ethyl butyl alcohol	4.5
2-Ethyl hexyl acetate	0.4
2-Ethyl hexyl alcohol	2.5
Ethyl butyrate	0.8
Ethyl ether	1.3
Ethyl ether of diethylene glycol	M
Ethyl ether of diethylene glycol acetate	M
Ethyl ether of ethylene glycol	M
Ethyl ether of ethylene glycol acetate	9.4
Ethyl lactate	M
Ethyl propionate	1.2
Ethylene chlorohydrin	M
Ethylenediamine	M
Ethylene dichloride	0.2
Ethylene glycol	M
Ethylene oxide	M
Fenchone	0.5
Furfural	4.8
Furfuryl acetate	insol.
Furfuryl alcohol	M
Glycol diacetate	21.2

TABLE 2.4.—*Continued*

Glycol monoacetate	M
Hercosol	insol.
Hi-Flash naphtha	insol.
n-Hexanol	6.5
Hexone (methyl isobutyl ketone)	2.81
Isobutyl acetate	1.64
Isobutyl alcohol	16.9 (25° C)
Isopropyl acetate	2.9
Isopropyl alcohol (anhydrous)	M
Isopropyl ether	0.7
Isopropyl ether of ethylene glycol	M
Isopropyl lactate	M
Mesityl oxide	2.85
Methanol (anhydrous)	M
3-Methoxy butyl acetate	3.7
Methyl acetate	11.0
Methyl acetoacetate	38.0
Methyl acetone	M
Methyl amyl acetate	0.9
Methyl amyl alcohol	6.4
Methyl n-amyl ketone	1.4
Methyl n-butyl ketone	2.2
Methylcyclohexone	3.0
Methyl ether of diethylene glycol	M
Methyl ether of diethylene glycol acetate	M
Methyl ether of ethylene glycol	M
Methyl ether of ethylene glycol acetate	M
Methyl ethyl ketone	11.8
Methyl n-hexyl ketone	0.6
Methyl propyl ketone	3.34
Mineral spirits	insol.
Monoacetin	M
Monochlorobenzene	insol.
Monoethanolamine	M
o-Dichlorobenzene	insol.
Petroleum naphtha	insol.
Pine oil	1.7
Pine oil (heavy)	2.4
Propylene chlorohydrin	M
Propylene dichloride	0.3
Propylene glycol	M
Propylene oxide	41.0
Safe-T-Esso	insol.
Solvesso No. 1	insol.
Solvesso No. 2	insol.
Solvesso No. 3	insol.
Tetrahydrofurfuryl alcohol	M
Tetrahydronaphthalene	insol.
Toluene	insol.
Turpentine (gum spirits)	insol.
Turpentine (steam distilled)	insol.
V. M. & P. naphtha	insol.
Xylene	insol.

S.S. = Slightly Soluble.
M = miscible.

Requirements of Diluents and Thinners

1. They should possess solvency.
2. They should have no harmful physiological effects.
3. The active and nonsolvents should be in such proportions as to impart maximum solvency.
4. They should approach the perfect mixture in solvent power, thinning qualities, blush resistance, rate of evaporation, low cost and nonlifting action of the undercoat.

References

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2. Calvert, R., *Ind. Eng. Chem.*, **21**, 213 (1929).
3. Sakurado, I., and Kido, I., *Cellulose Ind.* (*Tok.*), **9**, 238–46; (Summary in German), 27–33 (1933).
4. Davidson, J. G., *Ind. Eng. Chem.*, **18**, 670 (1926).
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Chapter 3

Vapor Pressure, Evaporation Rate, Boiling Point

No matter in what form it exists, matter exerts a vapor pressure. We are all familiar with the fact that liquid perfumes and certain solids, like camphor, menthol, naphthalene and other substances, expel odors, making it evident that their molecules have found the way to our olfactory nerves. We have also observed that ice and snow, at temperatures below the melting point of ice, will gradually disappear owing to evaporation. Even such solids as marble and quartz give off vapors; but they have such extremely low rates of evaporation that it would take countless centuries before a noticeable amount would disappear. Instruments available today are much too crude to measure such low rates of evaporation.

If we confine a liquid (e.g., alcohol or gasoline) in a closed vessel, molecules of the liquid will begin to leave the surface and accumulate in the air above it. This is caused by the kinetic action of the molecules of the liquid. The liberated particles now become typical gas molecules and exert a pressure on all sides of the container. Should we keep external forces constant and allow the alcohol to evaporate for a considerable time, a state of equilibrium would be reached wherein the number of molecules leaving the liquid would equal the number falling back into it. The pressure exerted by the molecules above the surface at equilibrium conditions is called the *vapor pressure* of a substance at a given temperature. This expression, in measured terms, indicates the tendency of a substance (usually liquid) to pass into a vapor.

If a liquid is not confined in a closed container, the vapors are carried away and the rate of evaporation is influenced by:

1. Temperature of the substance.
2. Temperature of surrounding area.
3. Rate of external heat supplied.
4. Conductivity of heat.
5. Specific heat of the substance.
6. Latent heat of evaporation.
7. Number and type of molecular aggregates.
8. Surface tension.

9. Presence of dissolved substances.
10. Atmospheric pressure.
11. Presence of water vapor (humidity).
12. Vapor pressure or pressures of the substance or substances under consideration.
13. Amount and rate of temperature depression.
14. Molecular weight of substances.
15. Method and speed in removal of vapors (wind, fans, etc.)
16. Depression of vapor pressure.
17. Viscosity.

Some of the rules for calculating vapor pressure:

1. Clapeyron's equation and modified forms.
2. Trouton's rule.
3. Hildebrandt curves.
4. Raoult's law.
5. Henry's law.

Although the properties of mixtures are not so well understood, there are indications that vapor pressure, evaporation rates and volatility are interrelated. A knowledge of these factors is essential in the separation of liquids by fractional distillation. This is especially true in the proper use of lacquers, varnishes and protective coatings. In the use of lacquers and other such products, interpretations cannot be made as adequately owing to the insufficient data available in the classification of solvents into low, medium, high, and midway boilers. Hofmann[2] has found that the rates of evaporation are not proportional to the boiling points and that hydroxyl groups in certain compounds retard the rate of evaporation. Alcohols evaporate more slowly than their corresponding esters of higher boiling points. Esters, ketones, alcohols and hydrocarbons having identical boiling points will have entirely different rates of evaporation because of the difference in chemical structure and the type of molecular aggregates formed. Hofmann[2] groups mixtures of solvents into two classes.

1. (a) Members of the same homologous series like ethyl, propyl, and butyl acetates, or benzene, toluene, and xylene.
   (b) Hydrocarbons and halogenated derivatives.
   (c) A hydrocarbon and an ester.

In the above cases, the solvents evaporate simultaneously at different rates and have no effect upon each other. When the more rapidly evaporating constituent is gone the remaining one evaporates at a constant rate.

2. The second group consists of constant-boiling mixtures formed by two dissimilar compounds, such as an alcohol and a hydrocarbon; these generally form constant-boiling mixtures at higher temperatures.

Stull[2a] has evaluated the vapor pressures of over 1200 organic compounds.

Anyone interested in this aspect of solvents should refer to this important critical survey.

Germann and Knight[3] have prepared a very interesting line coordinate chart on vapor pressure temperature (Fig. 3.2.).

A series of convenient nomographic charts of the vapor pressure of solvents have been prepared by Killeffer[4] (Figs. 3.3–3.6).

Othmer[5] has written an excellent treatise on the use of critical constants in correlating vapor pressure and latent heat. He claims to have worked out a simple relationship between reduced pressure and reduced latent heat; but from the study of the following graphs and nomograms, which are the results of his work, they can hardly be called simple (Figs. 3.7–3.10).

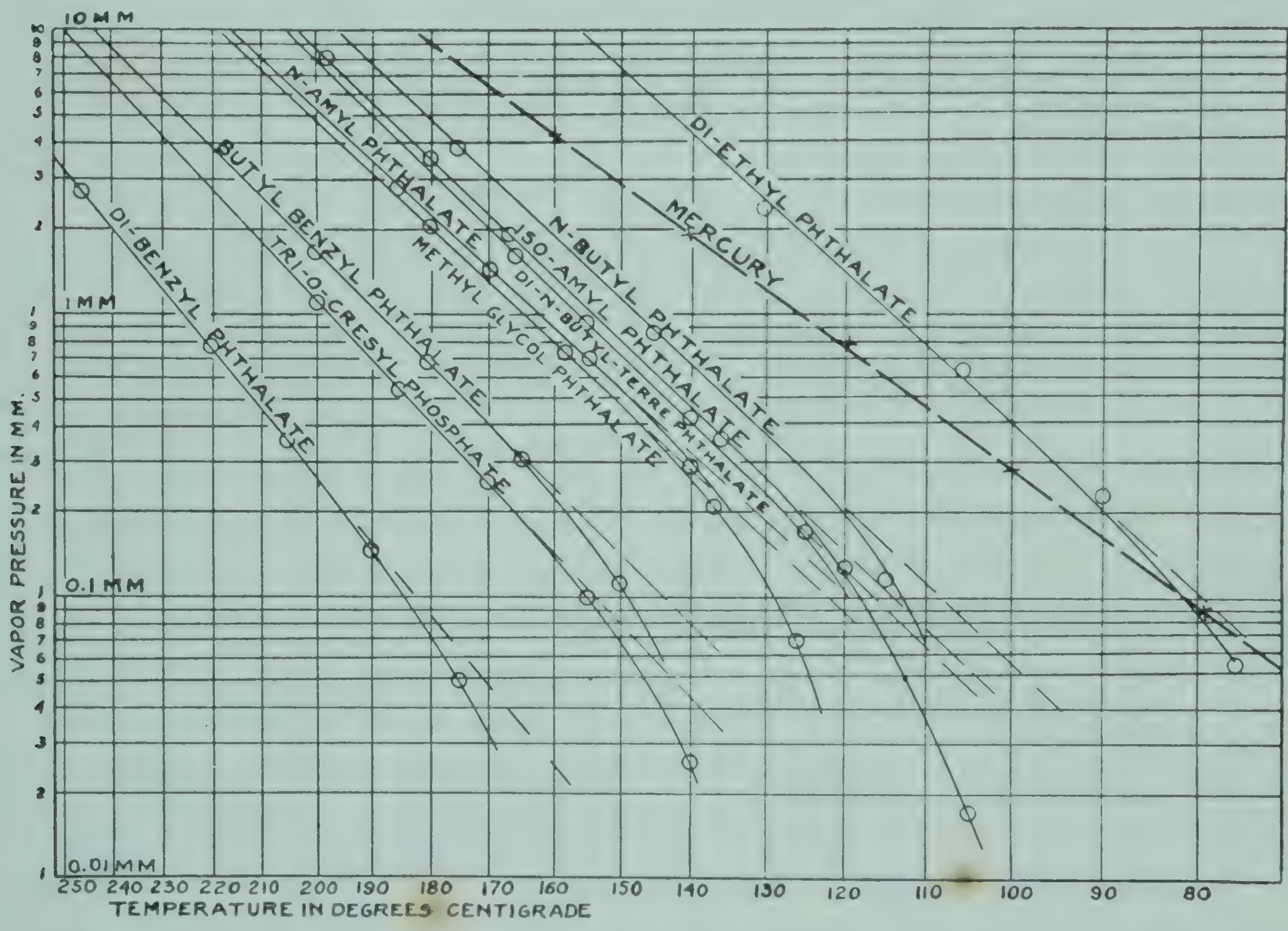


Figure 3.1. Vapor Pressure of Various Solvents at Different Temperatures.[1]

Azeotropic Mixtures

Azeotrope is a term applied to a mixture of two or more liquids which form loosely held molecular compounds and which have a fixed boiling point, generally lower than that of any of the component parts. This physical property is of fundamental importance in distillation since it plays a significant part in the processes of separation, isolation, concentration, and recovery. Horsley *et al.* have presented a series of tables and charts on azeotropes which is essential for those making a study of this subject.[6] Ewell, Harrison, and Berg have studied azeotropic distillation in great detail and have contributed to the concept of hydrogen bonds.

(*Text continued on page 56*)

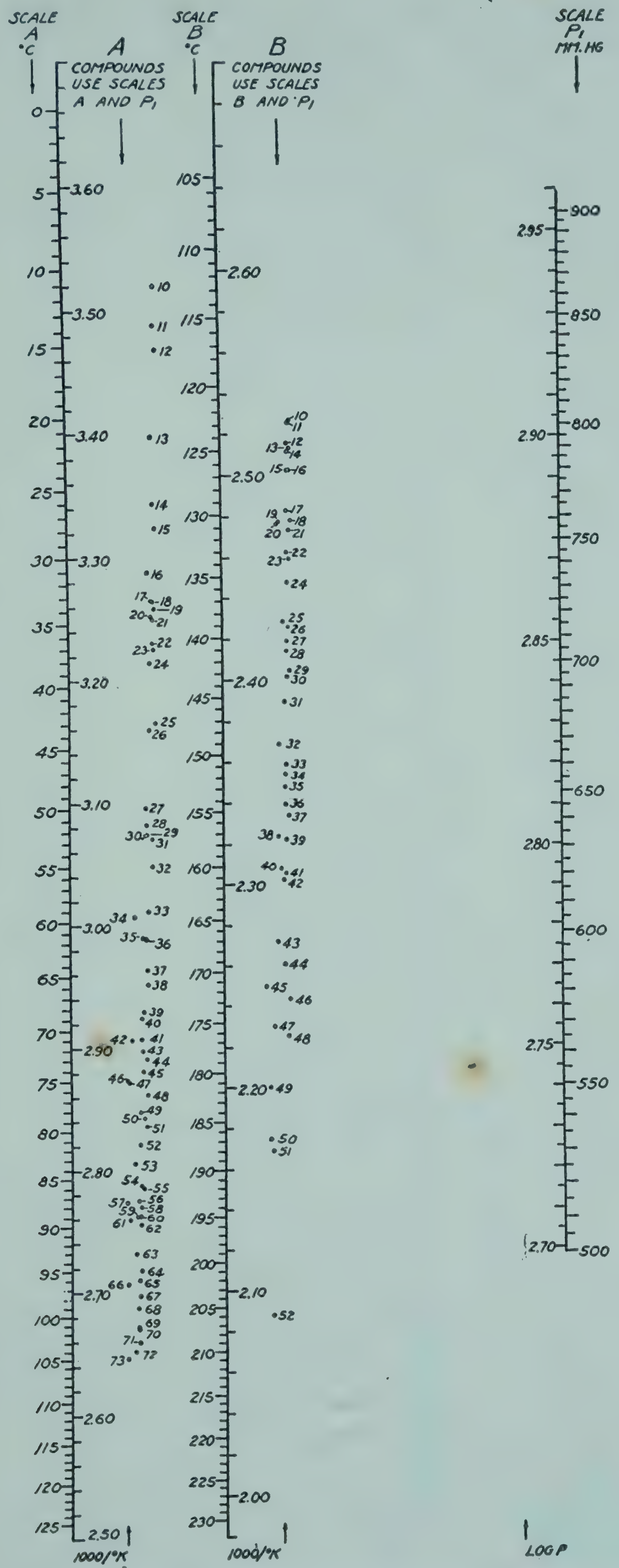
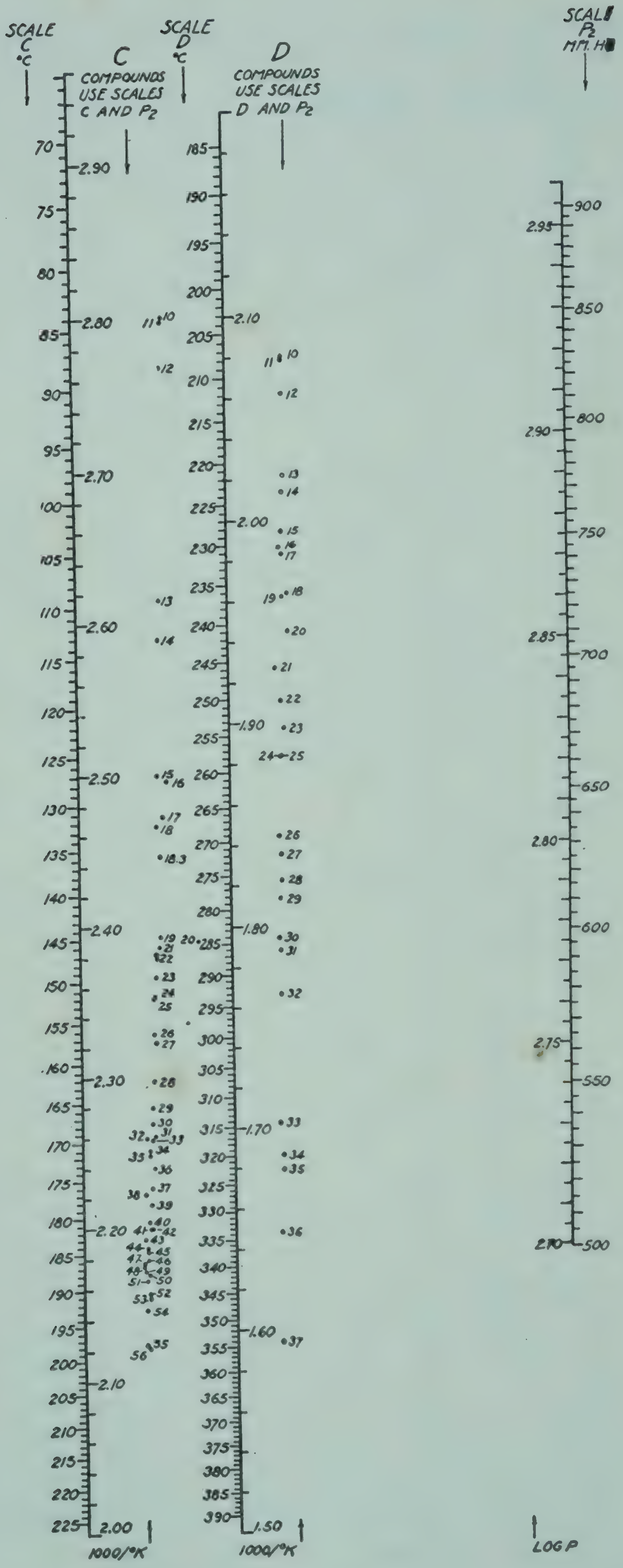


Figure 3.2. Boiling Points of Chain and Ring Compounds.[3]

(Continued on page 50–51)


SCALE C °C
C
COMPOUNDS USE SCALES C AND P2
SCALE D °C
D
COMPOUNDS USE SCALES D AND P2
SCALE P2 MM. H
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2.10
2.00
1.90
1.80
1.70
1.60
1.50
1000/°K
900
850
800
750
700
650
600
550
500
2.95
2.90
2.85
2.80
2.75
2.70
LOG P

Alphabetical Index to Boiling Point Chart

(A, B, C, and D refer to groups of compounds on the chart; numbers refer to compounds within these groups.)

Acenaphthene, D-26
Acetaldehyde, A-13
Acetic acid, A-72
Acetone, A-28
Acetophenone, C-46
n-Amyl alcohol, B-20
n-Amyl *n*-butyrate, B-44
n-Amyl formate, B-13
n-Amyl isobutyrate, B-42
n-Amyl *n*-propionate, B-36
Aniline, C-34
Anthracene, D-35
Anthraquinone, D-37

Benzaldehyde, C-29
Benzene, C-10
Benzoic acid, D-21
Benzonitrile, C-37
Benzophenone, D-32
Benzoyl chloride, C-41
Benzyl alcohol, C-51
Bromobenzene, C-22
α-Bromonaphthalene, D-27
m-Bromotoluene, C-33
o-Bromotoluene, C-30
p-Bromotoluene, C-31
o-Bromo-*p*-xylene, D-10
n-Butyl alcohol, A-73
tert-Butyl alcohol, A-47
sec-Butyl chloroacetate, B-40
n-Butyl formate, A-63
sec-Butyl formate, A-53
n-Butyric acid, B-38

Camphor, C-52
Carbazole, D-36
Carbon disulfide, A-25
Carbon tetrabromide, B-48
Carbon tetrachloride, A-39
m-Chloroaniline, D-15
o-Chloroaniline, C-53
Chlorobenzene, C-15
1,1-Chlorobromoethane, A-44
Chloroform, A-32
α-Chloronaphthalene, D-23
Chloropicrin, A-67
m-Chlorotoluene, C-24
o-Chlorotoluene, C-23
p-Chlorotoluene, C-25
m-Cresol, C-47
o-Cresol, C-38
p-Cresol, C-48
Cyclohexane, C-11
Cymene, C-28

n-Decane, B-35
Dibenzyl ketone, D-33
1,3-Dibromopropane, B-39
2,3-Dibromopropylene, B-26
1,2-Dichloroethane, A-45
Diethylaniline, C-55
Diethyl ether, A-17
Diïsobutyl, A-64
Diïsopropyl, A-31
Dimethylaniline, C-39
Dimethyl-*o*-toluidine, C-35
Dimethyl-*p*-toluidine, C-54
Diphenyl, D-22
Diphenylmethane, D-25
Dipropyl ether, A-50
Durene, C-40

Ethyl acetate, A-40
Ethyl alcohol, A-42
Ethyl aniline, C-50
Ethyl benzene, C-16
Ethyl bromide, A-22
Ethyl *n*-butyrate, B-11
Ethyl chloride, A-12
Ethylchloroacetate, B-28
Ethylene bromide, B-21
Ethylene glycol, B-50
Ethylene oxide, A-11
Ethyl formate, A-27
Ethylidene chloride, A-29
Ethyl iodide, A-37
Ethyl isobutyrate, A-65
Ethyl mercaptan, A-18
Ethyl propionate, A-56
Ethyl sulfide, A-51
Ethyl-*n*-valerate, B-23

Fluorene, D-31
Fluorobenzene, C-12
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Glycol diacetate, B-49

n-Heptane, A-55
n-Heptylic acid, B-52
Hexachloroethane, B-46
Hexamethyl benzene, D-24
n-Hexane, A-36
1-Hexene, A-33
Hydrogen cyanide, A-14

Iodobenzene, C-36
Isoamyl alcohol, B-19
Isoamyl formate, B-14
Isobutyl acetate, A-69
Isobutyl alcohol, A-66
Isobutyl benzene, C-26
Isobutyl-*n*-butyrate, B-34
Isobutyl formate, A-54
Isobutyl isobutyrate, B-30
Isobutyl-*n*-propionate, B-24
Isobutyl-*n*-valerate, B-41
Isobutyric acid, B-32
Isocaproic acid, B-51
Isodurene, C-42
Isopentane, A-15
Isopropyl acetate, A-49
Isopropyl alcohol, A-46
Isopropyl benzene, C-19
Isopropyl chloride, A-19
Isopropyl chloroacetate, B-31
Isopropyl formate, A-35
Isopropyl isobutyrate, B-10
Isovaleric acid, B-43

Mesitylene, C-20
Methyl acetate, A-30
Methyl alcohol, A-34
Methyl aniline, C-40
Methyl benzoate, C-43
Methyl butyrate, A-62
Methyl chloroacetate, B-17
Methylene chloride, A-24
Methyl ethyl ether, A-10
Methyl formate, A-16
Methyl isobutyrate, A-52
Methyl *n*-propionate, A-41
Methyl propyl ether, A-25
Methyl salicylate, D-14
Methyl sulfide, A-20
Methyl *n*-valerate, A-70

Naphthalene, C-56
α-Naphthol, D-29
β-Naphthol, D-30
Nitrobenzene, D-12

Nitromethane, A-59
m-Nitrotoluene, D-16
o-Nitrotoluene, D-13
p-Nitrotoluene, D-19
Nitro-*m*-xylene, D-20

n-Octane, B-16

Pentachloroethane, B-37
Pentamethylbenzene, D-17
n-Pentane, A-21
Phenanthrene, D-34
Phenol, C-32
Phthalicanhydride, D-28
Prehnitene, D-11
n-Propionic acid, B-25
n-Propyl acetate, A-60
n-Propyl alcohol, A-57
n-Propyl benzene, C-21
n-Propyl *n*-butyrate, B-27
n-Propyl chloride, A-26
n-Propyl formate, A-43
n-Propyl isobutyrate, B-22
n-Propyl *n*-propionate, B-12
n-Propyl *n*-valerate, B-33
Pseudocumene, C-27
Pyridine, C-14

Quinoline, D-18

1,1,1,2-Tetrachloroethane, B-18
sym-Tetrachloroethane, B-29
Tetrachloroethylene, A-71
Tetranitromethane, B-15
Toluene, C-13
m-Toluidine, C-49
o-Toluidine, C-44
p-Toluidine, C-45
1,1,1-Trichloroethane, A-38
1,1,2-Trichloroethane, A-68
Trichloroethylene, A-48

Urethane, B-45

n-Valeric acid, B-47

Water, A-61

m-Xylene, C-18
o-Xylene, C-18.3
p-Xylene, C-17

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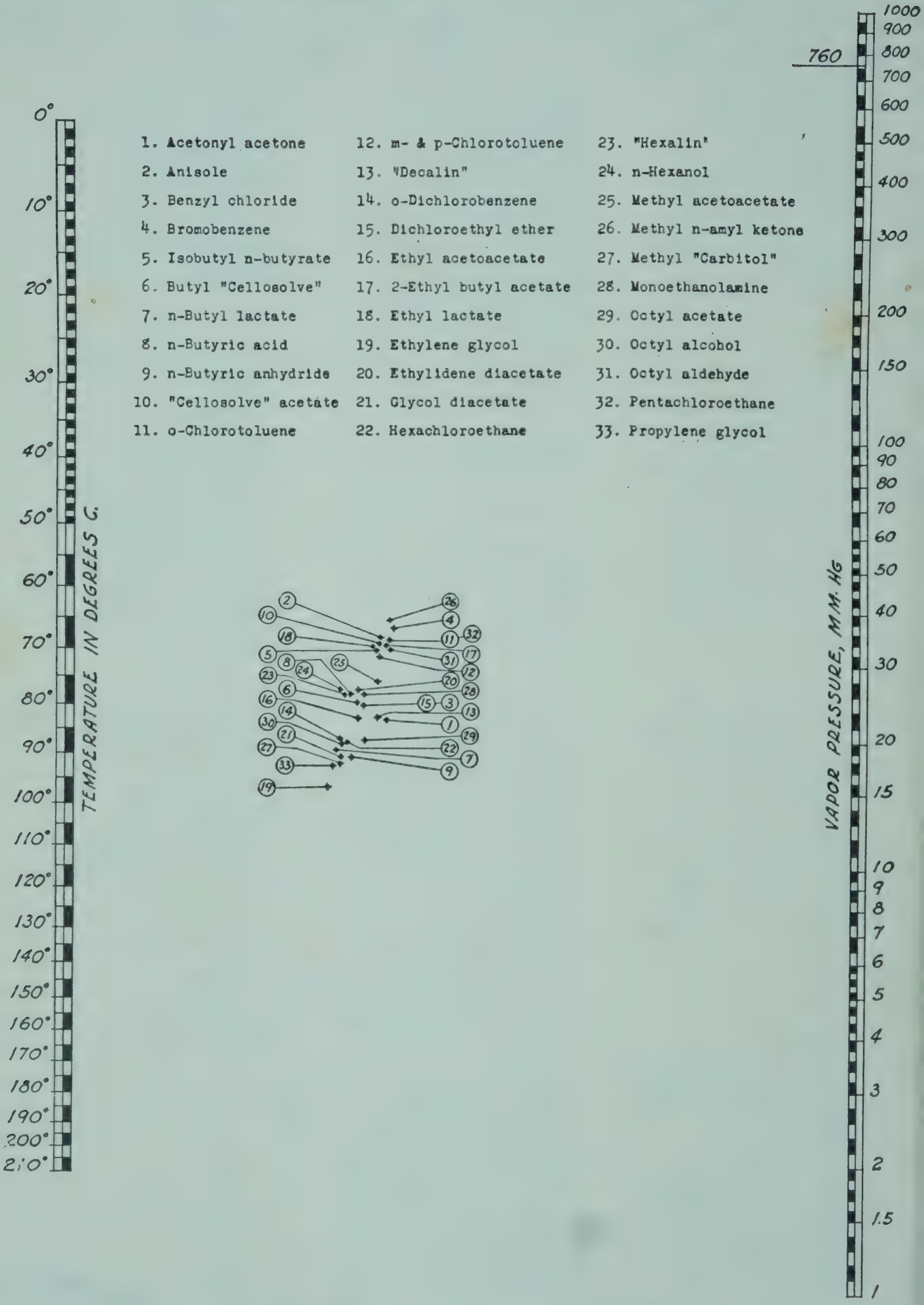


Figure 3.3. Vapor Pressures of Solvents Boiling between 150 and 200°C.[4]

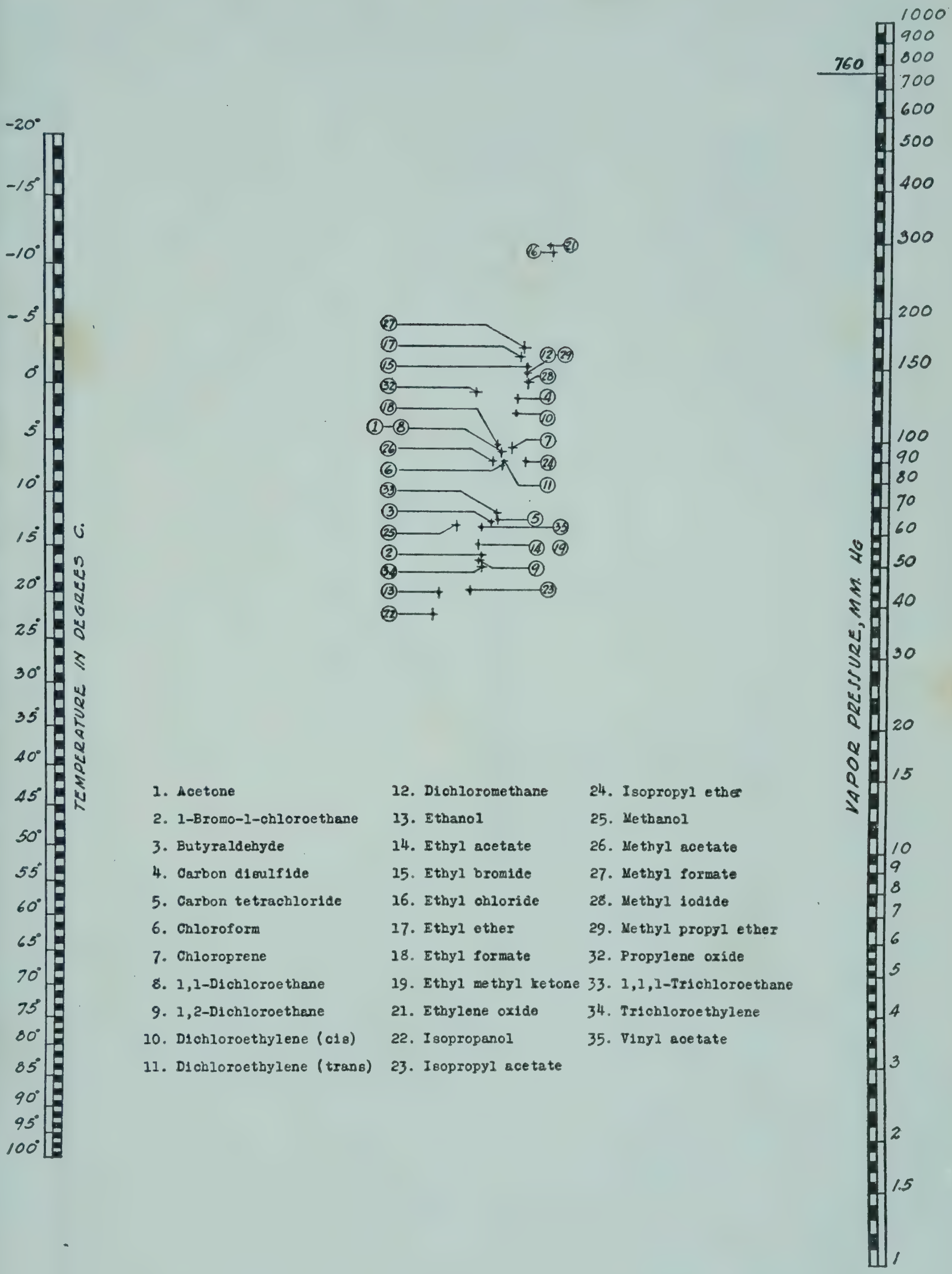
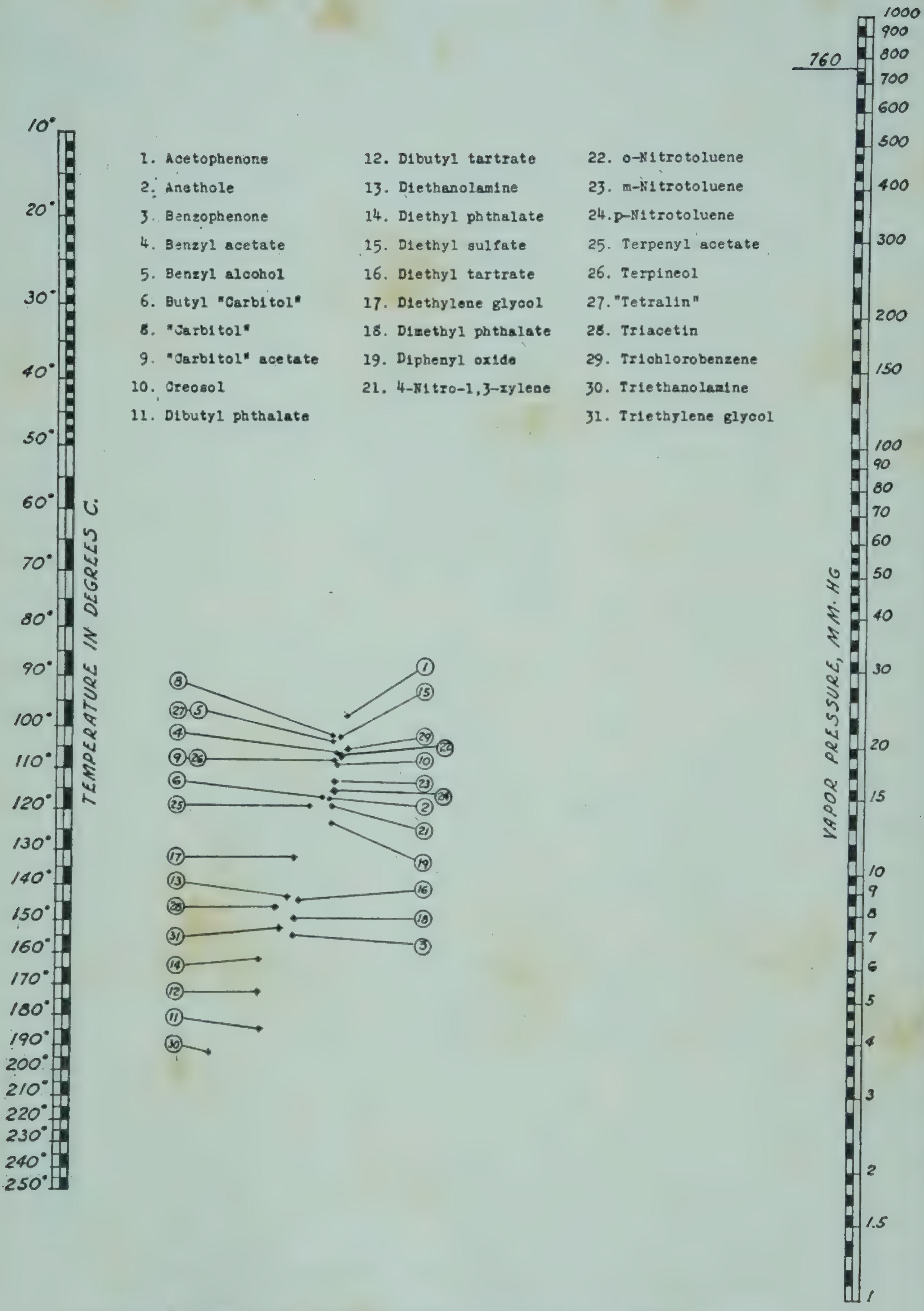


Figure 3.4. Vapor Pressures of Solvents Boiling below 90°C.[4]



1. Acetophenone
2. Anethole
3. Benzophenone
4. Benzyl acetate
5. Benzyl alcohol
6. Butyl "Carbitol"
8. "Carbitol"
9. "Carbitol" acetate
10. Creosol
11. Dibutyl phthalate
12. Dibutyl tartrate
13. Diethanolamine
14. Diethyl phthalate
15. Diethyl sulfate
16. Diethyl tartrate
17. Diethylene glycol
18. Dimethyl phthalate
19. Diphenyl oxide
21. 4-Nitro-1,3-xylene
22. o-Nitrotoluene
23. m-Nitrotoluene
24. p-Nitrotoluene
25. Terpenyl acetate
26. Terpineol
27. "Tetralin"
28. Triacetin
29. Trichlorobenzene
30. Triethanolamine
31. Triethylene glycol

TEMPERATURE IN DEGREES C.
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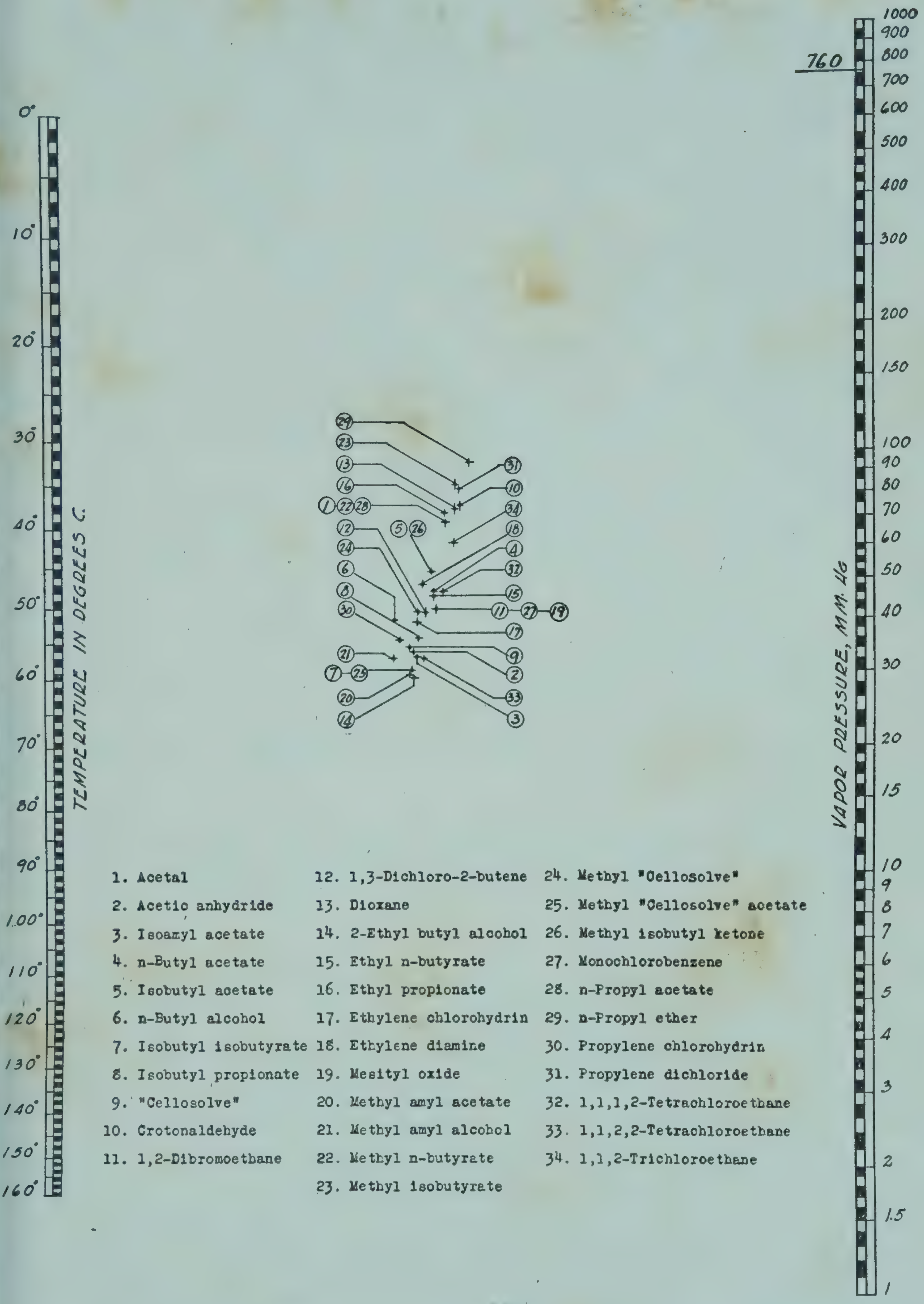
Figure 3.5. Vapor Pressures of Solvents Boiling at 200°C and above.[4]



1. Acetal
2. Acetic anhydride
3. Isoamyl acetate
4. n-Butyl acetate
5. Isobutyl acetate
6. n-Butyl alcohol
7. Isobutyl isobutyrate
8. Isobutyl propionate
9. "Cellosolve"
10. Crotonaldehyde
11. 1,2-Dibromoethane
12. 1,3-Dichloro-2-butene
13. Dioxane
14. 2-Ethyl butyl alcohol
15. Ethyl n-butyrate
16. Ethyl propionate
17. Ethylene chlorohydrin
18. Ethylene diamine
19. Mesityl oxide
20. Methyl amyl acetate
21. Methyl amyl alcohol
22. Methyl n-butyrate
23. Methyl isobutyrate
24. Methyl "Cellosolve"
25. Methyl "Cellosolve" acetate
26. Methyl isobutyl ketone
27. Monochlorobenzene
28. n-Propyl acetate
29. n-Propyl ether
30. Propylene chlorohydrin
31. Propylene dichloride
32. 1,1,1,2-Tetrachloroethane
33. 1,1,2,2-Tetrachloroethane
34. 1,1,2-Trichloroethane

Figure 3.6. Vapor Pressures of Solvents Boiling between 90 and 150°C.[4]

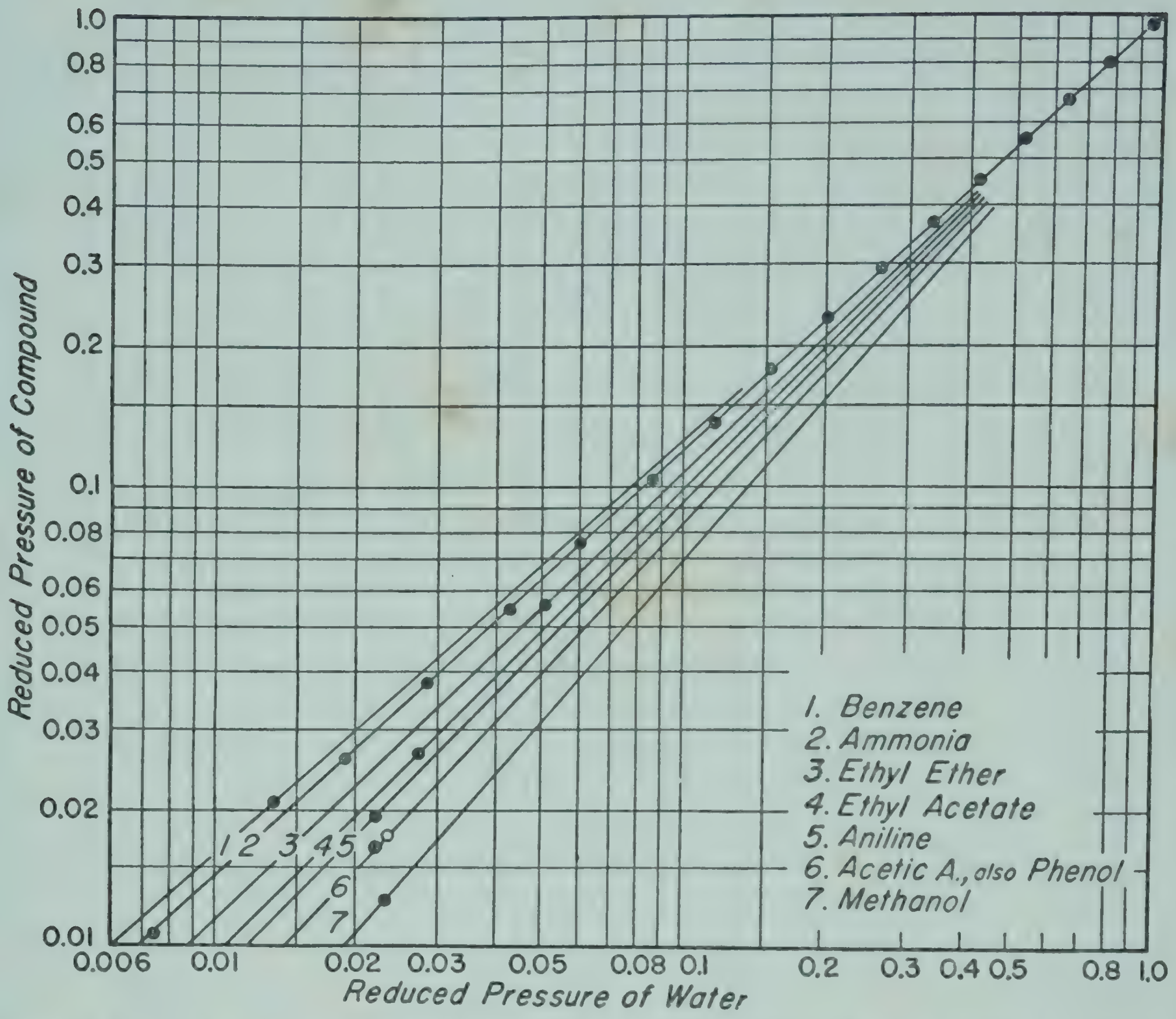


Figure 3.7. Logarithmic Plot of Reduced Vapor Pressures of Several Compounds Against Reduced Vapor Pressures of Water, Always at the Same Reduced Temperatures.[5]

Basically the strength of the hydrogen bond varies, depending upon the atoms between which the hydrogen is coordinating, as follows:

Strong

O → HO

N → HO

O → HN

Weak

N → HN

$$\left.\begin{array}{l} \mathrm{O} \\ \\ \\ \mathrm{N} \end{array}\right] \begin{array}{l} \rightarrow \\ \\ \\ \rightarrow \end{array} \left[\begin{array}{l} \mathrm{HCCl_2} \\ \mathrm{HCCl—CCl} \\ \mathrm{HCNO_2} \\ \mathrm{HCCN} \end{array}\right.$$

These investigators have classified liquids into the following groups:

"Class I. Liquids capable of forming three-dimensional networks of strong hydrogen bonds—e.g., water, glycol, glycerol, amino alcohols, hydroxylamine hydroxy acids, polyphenols, amides, etc. Compounds such as nitromethane and acetonitrile also form three-dimensional networks of hydrogen bonds, but the bonds are much weaker than those involving OH and NH groups. Therefore, these types of compounds are placed in class II.

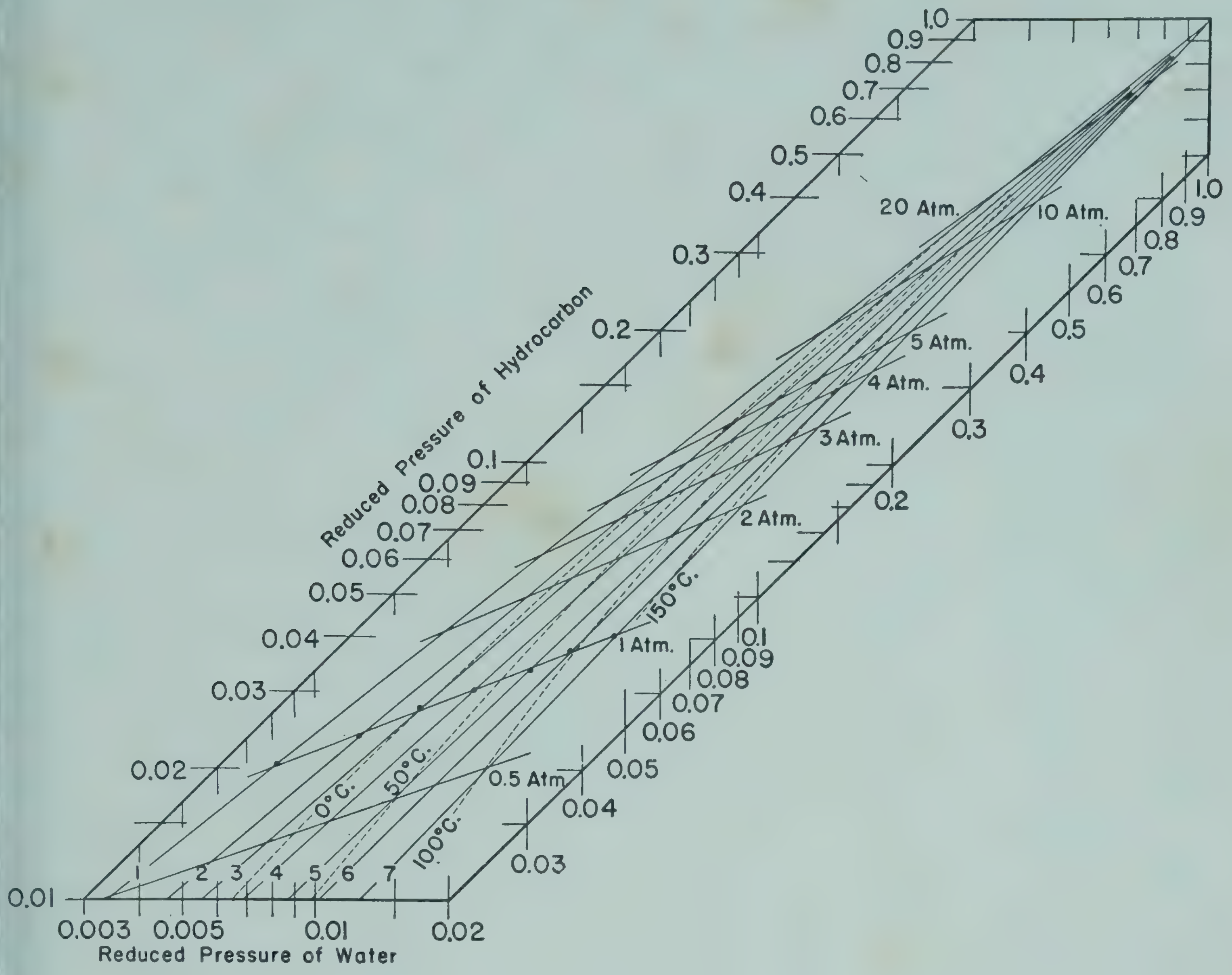


Figure 3.8. Logarithmic Plot of Reduced Vapor Pressures of Lower Hydrocarbons.[5] 1, ethane; 2, propane; 3, butane; 4, pentane; 5, hexane; 6, heptane; 7, octane. Cross lines are isobars (constant normal pressure) and are straight; dotted curves are isotherms (constant normal temperature).

"Class II. Other liquids composed of molecules containing both active hydrogen atoms and donor atoms (oxygen, nitrogen, and fluorine)—e.g. alcohols, acids, phenols, primary and secondary amines, oximes, nitro compounds with α-hydrogen atoms, nitriles with α-hydrogen atoms, ammonia, hydrazine, hydrogen fluoride, hydrogen cyanide, etc.

"Class III. Liquids composed of molecules containing donor atoms but no active hydrogen atoms—e.g., ethers, ketones, aldehydes, esters, tertiary amines (including pyridine type), nitro compounds and nitriles without α-hydrogen atoms, etc.

"Class IV. Liquids composed of molecules containing active hydrogen atoms but no donor atoms. These are molecules having two or three chlorine atoms on the same carbon as a hydrogen atom, or one chlorine on the same carbon atom and one or more chlorine atoms on adjacent carbon atoms—e.g., $CHCl_3$, CH_2Cl_2, CH_3CHCl_2, $CH_2Cl—CH_2Cl$, $CH_2Cl—CHCl—CH_2Cl$, $CH_2Cl—CHCl_2$, etc.

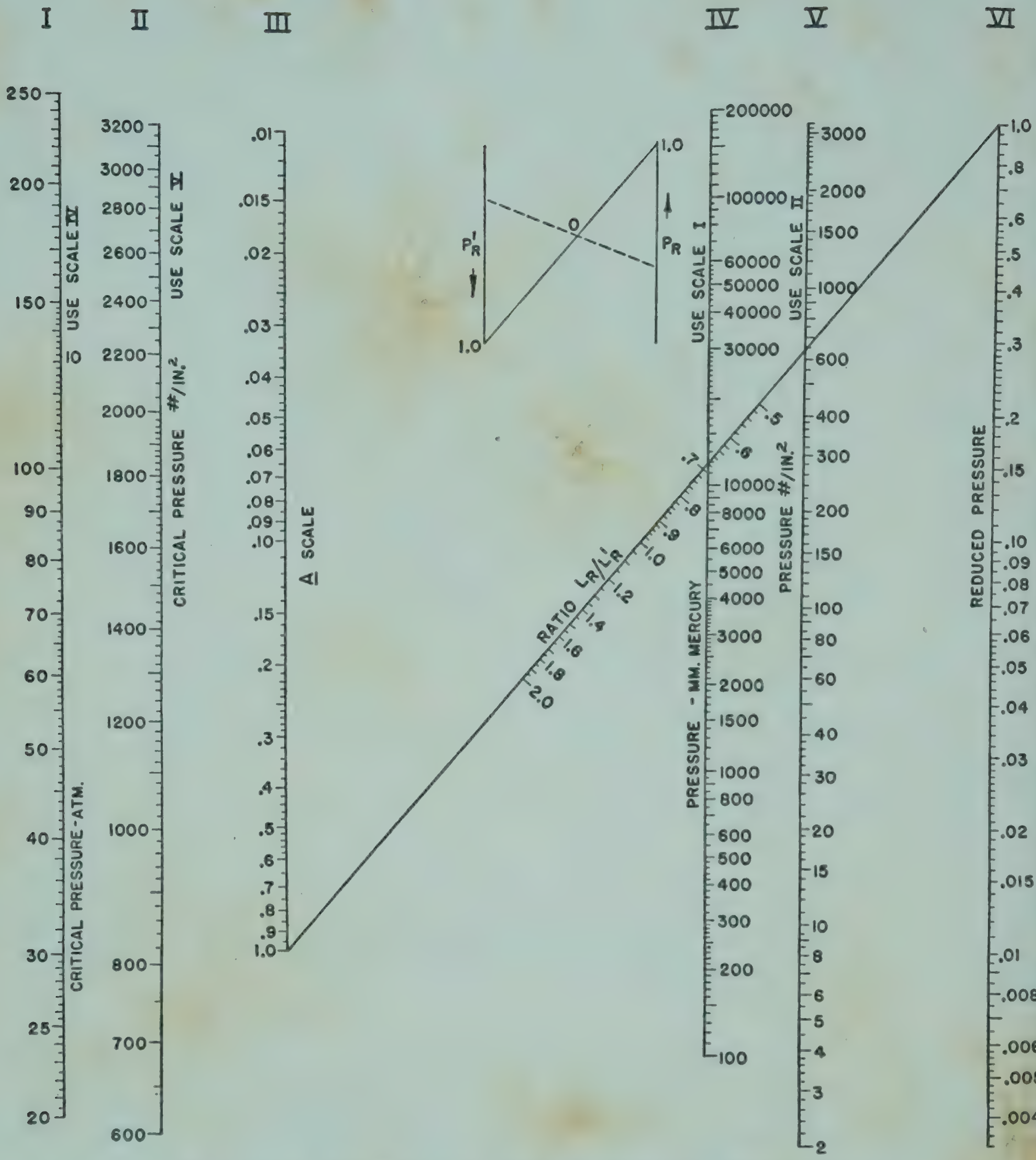


Figure 3.9. Pressure and Reduced Pressure Nomogram.[5]

A straight line through a point on critical pressure scale I (or II) and pressure scale IV (or V) gives value of reduced pressure on scale VI. A straight line through value of reduced pressure of water on scale *A* and value of ratio L_R/L'_R on diagonal scale gives value of reduced pressure on scale VI.

"Class V. All other liquids—i.e., liquids having no hydrogen-bond-forming capabilities—e.g., hydrocarbons, carbon disulfide, sulfides, mercaptans, halohydrocarbons not in class IV, non-metallic elements such as iodine, phosphorus, sulfur, etc.

"Classes I and II include the liquids usually called 'associated' or 'abnormal' liquids. The concept of associated liquids has been based on deviations from certain physicochemical relations, such as the Ramsay-Shields

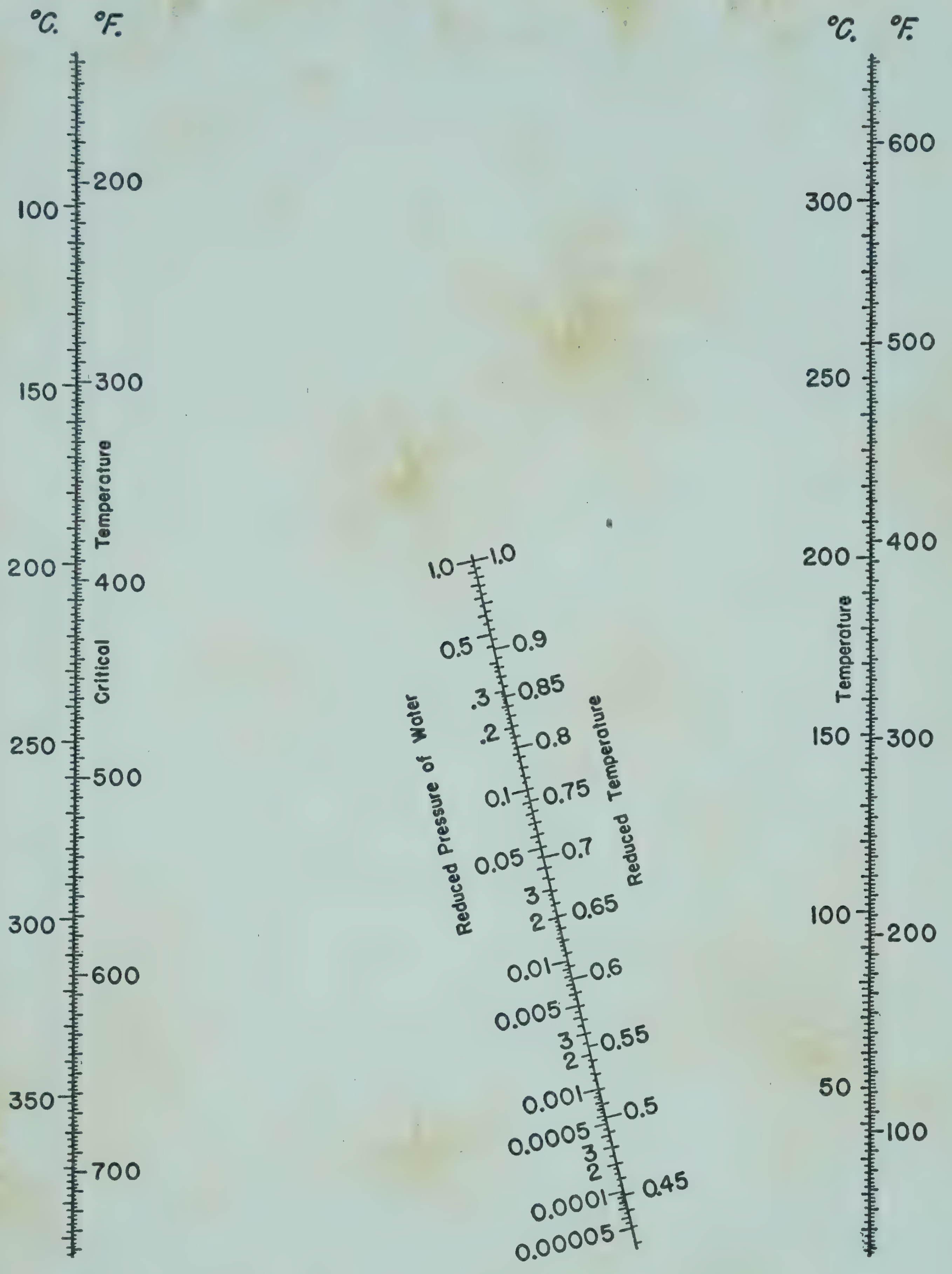


Figure 3.10. Temperature and Reduced Temperature Nomograph.[5]

A straight line through a value of critical temperature on the left-hand scale and a value of the normal temperature on the right-hand scale gives a value of reduced temperature, T_R, on the diagonal scale. This value of T_R corresponds with a value of the reduced pressure of water in the calibrations on the other side of the diagonal scale.

surface tension equation, Trouton's rule, etc., which are obeyed by normal liquids like hydrocarbons, carbon tetrachloride, etc. No explanation of, or mechanism for, the association was given until the advent of the hydrogen bond concept, although the general relation to the presence of OH and NH groups had been recognized for some time. The term 'hydrogen-bonded liquid' should now replace 'associated liquid,' although the term 'association' should still prove useful to describe the general phenomenon. Class I and class II liquids have relatively high dielectric constants.

"Classes I, II, and III include water-soluble substances. In general, any liquid (or solid) that can form hydrogen bonds with water will dissolve in water (or tend to dissolve in water). Class II liquid—*e.g.*, alcohols—can form hydrogen bonds with water in two ways: from oxygen of water to hydrogen of alcohol, and from oxygen of alcohol to hydrogen of water. Class III liquids—*e.g.*, ketones—can form hydrogen bonds with water in only one way: from oxygen of ketone to hydrogen of water. While all class II and class III liquids tend to dissolve in water, the extent to which they actually do dissolve depends on how many CH_2 groups have to be pulled into solution by the hydrogen-bond-forming groups. For instance, the lower alcohols are completely soluble in water—*n*-butyl about 10%, *n*-amyl about 3%, etc. When the hydrocarbon part of the molecule is so large that the solubility is very small—e.g., decyl alcohol—the tendency of the hydrogen-bond-forming group to dissolve in water causes the liquid to form a monomolecular oriented layer on the water surface. Ethyl ether is soluble in water only about 7%, but it has four CH_2 groups to pull into solution just as *n*-butyl alcohol does. However, methyl ether with only two CH_2 groups and dioxane with four CH_2 groups, but two ether oxygens, are completely soluble in water. Even high-molecular-weight substances, such as carbohydrates, proteins, gums, and other hydrophilic materials, are soluble in water since they can form many hydrogen bonds per molecule."

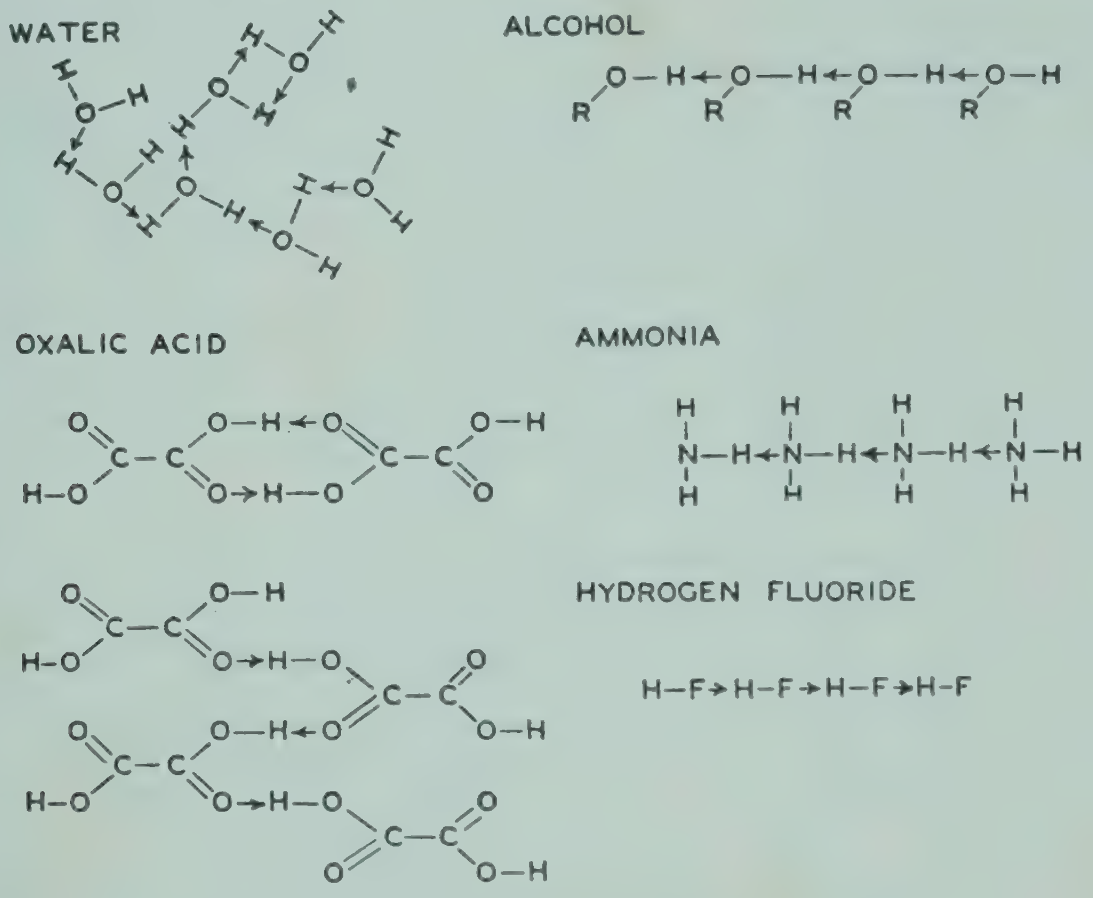


Figure 3.11. Concept of Hydrogen Bonds.

Before one component of a constant-boiling mixture can be removed it is necessary that an entrainer be added to the azeotropic distillation. Here again Ewell, Harrison and Berg[6a] have generalized their description of the effect of the added entrainer.

"Class IV liquids might be expected to be soluble in water, but the hydrogen bonds formed between water and these liquids (from oxygen of water to active hydrogen of class IV liquid) would be quite weak and do not compensate for its water hydrogen bonds which are broken.

"Class V liquids are all very insoluble in water, since many of the water hydrogen bonds would have to be broken to make room for the class V molecules and no compensating hydrogen bonds are formed.

TABLE 3.1. SUMMARY OF DEVIATIONS FROM RAOULT'S LAW[6]

CLASSES	DEVIATIONS	HYDROGEN BONDING
I + V	Always + deviations; I + V, frequently limited solubility	H bonds broken only
II + V		
III + IV	Always − deviations	H bonds formed only$_2$
I + IV	Always + deviations; I + IV, frequently limited solubility	H bonds both broken and formed, but dissociation of class I or II liquid is more important effeci
II + IV		
I + I	Usually + deviations, very complicated groups, some − deviations give some max. azeotropes	H bonds both broken and formed
I + II		
I + III		
II + II		
II + III		
III + III	Quasi-ideal systems, always + deviations or ideal; azeotropes, if any, will be minima	No H bonds involved
III + V		
IV + IV		
IV + V		
V + V		

"By this system of classification it is possible to predict the nature of the deviations from Raoult's law, and the hydrogen bonding in a mixture makes it possible to judge approximately the extent of these deviations. The acutal formation of an azeotrope or constant-boiling mixture depends upon (*a*) the magnitude of the deviations from Raoult's law and (*b*) the difference in boiling point between the two pure components. The smaller the deviations from Raoult's law for a pair of substances, the smaller the difference in boiling point must be before an azeotrope will form (Fig. 3.12).

"When a system which shows positive (+) deviations from Raoult's law forms an azeotrope, it will be a minimum-boiling azeotrope. When the deviations are negative (−), the azeotrope, if formed, will be maximum-boiling. These rules may be exemplified by the following actual cases.

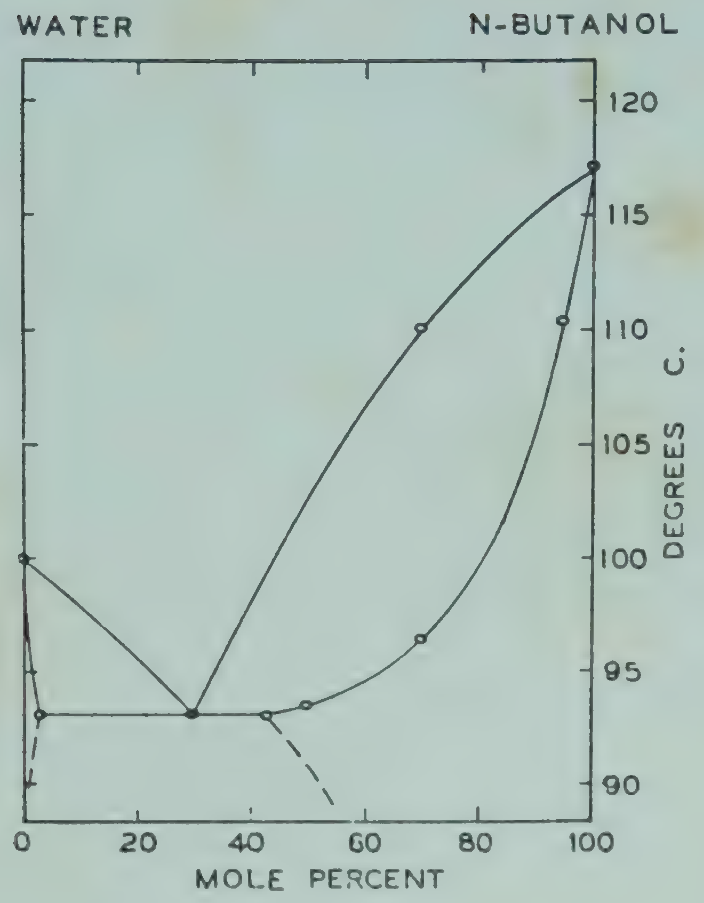


Figure 3.12. Diagram of a Heterogeneous Azeotrope, Water-*n*-Butanol.

"An example of II + V is ethanol (class II) and benzene (class V) which gives a minimum azeotrope boiling at 68.2° and containing 44.8 mole % ethanol.

"An example of III + IV is acetone (class III) and chloroform (class IV) which gives a maximum azeotrope boiling at 64.5° and containing 34.5 mole % acetone.

"Boiling point relations for water solutions are well known. The minimum constant-boiling mixture, ethanol-water, boiling at 78.1° and yielding 89.2 mole % ethanol, is an example of I + II. The minimum constant-boiling mixture 1,4-dioxane-water, boiling at 87.8° and having a composition of 47 mole % dioxane (*13*), is an example of I + III. Water forms a few maximum azeotropes with certain compounds—for instance, with formic acid, ethylenediamine, and hydrazine. Water also forms maximum azeotropes with the strong acids—hydrochloric, hydrobromic, hydriodic, and nitric. Because of the insolubility of class IV and class V liquids in water, heterogeneous or two-phase minimum azeotropes are invariably formed by these classes of compounds with water.

"An example of II + III is methanol (class II) and acetone (class III) which gives a minimum azeotrope boiling at 54.6° and containing 14 mole % methanol. The dissociation of the methanol is the principal effect.

"An example of binary mixtures consisting of class II and class IV liquids is methanol (class II) and chloroform (class IV) which yields a minimum azeotrope boiling at 53.5° and containing 35 mole % methanol.

"All combinations of class III, IV, and V liquids, except III + IV, are quasi-ideal solutions and only occasionally show a minimum azeotrope. They occur when the boiling points of the two constituents are very close.

An example of III + V which gives a minimum azeotrope is acetone (class III) and *n*-hexane (class V), boiling at 49.8° and containing 68 mole % acetone. An example of two class V liquids forming a minimum azeotrope is benzene-methylcyclopentane boiling at 71.4° and containing 90 mole % methylcyclopentane. These azeotropes are caused by internal pressure differences."

"1. Water + strong acids—e.g., water + HCl, HBr, HI, HNO_3.

2. Water + certain associated liquids—e.g., water + formic acid, hydrazine, ethylenediamine.

3. Donor liquids (class III) + non-associated liquids containing active hydrogens (class IV)—e.g., acetone + chloroform, cyclohexanone + bromoform, butyl acetate + 1,2,2-trichloropropane.

4. Organic acids + amines—e.g., acetic acid + triethylamine, propionic acid + pyridine.

5. Phenols + amines—e.g., phenol + aniline, *o*-cresol + dimethylaniline.

6. Organic acids + donor liquids containing oxygen—e.g., formic acid + diethyl ketone, butyric acid + cyclohexanone.

7. Phenols + donor liquids containing oxygen—e.g., phenol + methylhexylketone, *o*-cresol + ethyloxalate.

8. Phenols + alcohols—e.g., phenol + *n*-octanol, *o*-cresol + glycol.

"1. To separate a closely boiling pair or a maximum azeotrope:
   a. The entrainer forms a binary minimum azeotrope with only one component.
   b. The entrainer forms binary minimum azeotropes with each component, but one minimum is sufficiently lower than the other.
   c. The entrainer forms a ternary minimum azeotrope which is sufficiently lower than any binary azeotropes. The ratio of the original components in the ternary must be different from their ratio before the entrainer was added.

"2. To separate a minimum azeotrope:
   a. The entrainer forms a binary minimum azeotrope with one component which is sufficiently lower than the original minimum azeotrope.
   b. The entrainer forms a ternary minimum azeotrope which is sufficiently lower than any binary minimum azeotrope and in which the ratio of the original components is different from their ratio in the binary minimum azeotrope.

"Entrainers suitable for the separation of close-boiling hydrocarbon mixtures show the following desirable properties:

1. Boil within a limited range (0–30° C.) of the hydrocarbon which it is desired to separate.

2. Form, on mixing with the hydrocarbon a large positive deviation from

Raoult's law, to give a minimum azeotrope with one or more of the hydrocarbon types in the mixture.

3. Be soluble in the hydrocarbon at the distillation temperature and for some degrees below it.
4. Be easily separated from the hydrocarbons with which it forms an azeotrope.
5. Be inexpensive and readily obtainable.
6. Be stable at the distillation temperature.
7. Be nonreactive with the hydrocarbons or the column material."

"Rates of evaporation are accelerated by the corresponding increase in vapor pressure which is brought about by the formation of azeotropic mixtures. A higher rate of evaporation causes excess chilling. In coatings of lacquer, varnish, or paint, where the depth of the solution is small, blush or precipitation may occur. If the azeotropic mixture consists of a solvent and a nonsolvent, these two substances, in evaporating, leave the solution as one substance. It follows, therefore, that should a larger quantity of the active solvent, in these and other mixtures, leave before the nonsolvent, precipitation or blush will take place. To prevent this undesirable occurrence an excess of nonsolvent, of the type that will evaporate at an early stage in the process, should be used in the solution or care should be taken not to mix liquids which are likely to form azeotropic mixtures. With the addition of medium- or high-boiling solvents, the vapor pressure is reduced and the rate of evaporation is consequently retarded. This reduction in the rate of evaporation is accordingly dependent upon the evaporation rate of each constituent in the solution, the amounts present, and the molecular aggregates formed. The vapor pressure is a function of the size of the molecule; this is shown by the fact that of two substances with the same boiling point, the one with the lower molecular weight will cause a larger reduction in evaporation rates. The function of a mixture where azeotropic properties are not present is determined by its vapor, and by the amounts of the constituents."

The rate of evaporation of a drying film of varnish, paint or lacquer becomes progressively slower. This is because the secondary bonds of attraction are set free momentarily when the volatile solvent leaves the molecular aggregate. These temporarily free secondary valence bonds exert their force on the remaining aggregates and knit the constituent parts closer and more firmly. These stronger bonds of attraction consequently retard the rate of evaporation. Vaporization results in loss of energy with consequent drop in temperature. The rate is governed by the specific heat of the substance, latent heat of evaporation, heat of conductivity, and the rate of heat that is supplied. Wilson[7] states that the drop in temperature is a function of the vapor pressure and the latent heat of evaporation when other variables are held constant.

Determinations of blush resistance are similar to dilution ratio values, with the one difference that blush measurements are made with blush-producing liquids rather than with precipitants as is the case with dilution ratio determinations. Such solvents as ethyl lactate, diacetone, ethyl alcohol, chlorohydrin, and other high-boiling solvents which retain their solubility in the presence of a small quantity of water diminish evaporation rate, and prevent or delay blush, precipitation, or chilling. King and Smedley[8] developed a method for detecting constant-evaporating mixtures by means of the Abbé refractometer. They discovered a mixture of chloroform and alcohol which will evaporate at a constant rate, and more rapidly than either component. They classified solvent mixtures into two groups, one of which forms an ideal mixture with normal properties and the other exhibits abnormal properties.

Generally the addition of one solvent to another produces a gradual increase in vapor pressure until the maximum is reached when, at this point, there is an accompanying fall. There are many instances, however, where the reverse is true; for example, the gradual addition of acetone to chloroform produces a diminution of vapor pressure until a minimum is reached, after which an increase becomes evident. Upper and lower limits are governed by the percentages of constituents in the mixture.

Hofmann[2] has correlated evaporation and distillation curves with the following interpretations:

1. Straight evaporation curves and straight (flat) distillation curves are possible only with pure compounds.
2. Curved evaporation curves and flat distillation curves indicate constant-boiling mixtures.
3. Curved evaporation and distillation curves show the behavior of the so-called ideal mixture of similar compounds.
4. Straight evaporation curves and curved distillation curves are indicative of constant-evaporating mixtures.

Gardner's[11] work on the evaporative index has simplified the Maxwell-Stefan equation for the rate of evaporation on a liquid surface at a definite point (see Table 3.5, page 88):

$$E = K\ (D_1 M p_{At})$$

where E = evaporation rate in grams per hour per sq cm
K = the group ($R \quad T \quad P \quad x$)
D_1 = diffusion coefficient at 1 atm pressure
M = molecular weight
p_{At} = vapor pressure of evaporating liquid (mm Hg)
R = gas constant (82.07 cc/atm)
T = absolute temperature (° K)
x = distance in cm in direction of diffusion through stagnant film
α = proportionality constant

Kinney[13, 14] has devised a method for correlating the structure of organic compounds with their boiling points. He has worked out boiling-numbers for a variety of atoms, groups, and molecules. This work was brought about by a realization that the boiling point of a compound is determined by its molecular structure. While it is true that the boiling point of a substance is also affected by the dipole moment, hydrogen bonds, and association, they too are dependent upon the kind, number, and arrangement of the atoms and therefore play a secondary role.

"Practically all organic compounds may be considered to be derivatives of the normal paraffin hydrocarbons or of hydrogen. Consequently, these were taken to be the basis of the system. Next, various values were assigned to carbon and hydrogen, and the absolute boiling points of hydrogen and the normal paraffin hydrocarbons were plotted against the cube root of the sum of the different atomic numbers assigned to carbon and hydrogen. In this way it was possible to choose those values of carbon and hydrogen which cause the boiling point of molecular hydrogen to coincide most closely with the straight line of the hydrocarbon plot, thus making it possible to compare derivatives of hydrogen and of the normal paraffin hydrocarbons. The best values of carbon and hydrogen are 0.8 and 1.0 unit, respectively, and may be called the atomic boiling point numbers (B.P.N.) for these atoms. Also the equation for the hydrogen-hydrocarbon plot may be used for correlating the boiling points of derivatives of hydrogen and the normal hydrocarbons with the boiling points of those substances themselves. Two forms of this equation are given below in which B.P. is the boiling point in degrees centigrade and B.P.N. (molecular boiling point number) is the sum of the individual atomic and group boiling point numbers expressing the structure of the molecule.

$$\text{B.P.} = 230.14 \sqrt[3]{\text{B.P.N.}} - 543 \tag{1}$$

$$\text{Log B.P.N.} = 3[\log(\text{B.P.} + 543) - 2.3620] \tag{2}$$

"The boiling point number (B.P.N.) of derivatives of hydrogen or of the normal hydrocarbons may be considered to be composed of two parts: that due to the hydrogen atom or the hydrocarbon residue and that due to the characteristic atom or group. The latter value may be determined readily as the difference between the boiling number for the hydrogen atom or the hydrocarbon residue and the molecular boiling point number determined from the boiling point. For example, the branched chain hydrocarbons are considered to be alkyl derivatives of the normal hydrocarbons and the molecular boiling point number the sum of the atomic boiling point numbers for the hydrogen and carbon atoms in the normal chain plus the boiling point number which has been determined for the alkyl group.

"The boiling point number of the methyl group was determined from the following data, which demonstrates the method. The boiling point of 2-

methylbutane is 28°C, which gives an observed B.P.N. of 15.27. In the butane chain there are four carbon atoms which contribute 3.2 and nine hydrogens which contribute 9.0 units. The difference of 3.07 units is to be attributed to the side chain methyl group. As an approximation a value of 3.05 has been adopted as the B.P.N. of the side chain methyl group, which gives a calculated B.P.N. of 15.25 and a boiling point of 27.75°."[13]

"The calculation of the boiling points of the aliphatic hydrocarbons may be accomplished by the use of the boiling point equation developed previously. The method is empirical and depends upon obtaining sufficient accurate boiling point data so that the boiling point number (B.P.N.) may be obtained for the various structural groupings. From the existing data for the aliphatic hydrocarbons it is possible to obtain the necessary boiling point numbers and to calculate the boiling points of these hydrocarbons, including the naphthenes, from their structures with an accuracy of better than 5 per cent in most cases. The structure of a hydrocarbon may also be calculated from its boiling point and molecular formula, but for the higher hydrocarbons which have large numbers of isomers, several structures have the same molecular boiling point number (B.P.N.) and it is impossible to make a further limitation. In spite of this difficulty, the use of boiling point data limits definitely the possible structures which a hydrocarbon boiling at a particular temperature may have and should, therefore, be a valuable tool for the petroleum chemist."

Boiling Point of Paraffin Hydrocarbons

"The calculation of the boiling point of a paraffin hydrocarbon involves simply the summation of the B.P.N.'s of the carbon and hydrogen atoms in the longest chain in the molecule together with the B.P.N.'s of any radicals attached or any special arrangements of them. It is essential that the longest chain in the molecule be taken as the main chain because the boiling point in part is a function of the length of the molecule. The resulting calculated B.P.N. is inserted into the boiling point equation and the equation solved for B.P., the calculated boiling point. As an example of how the boiling point of a paraffin hydrocarbon is calculated, 2,2-dimethylpentane may be considered. The summation of the B..N.'s in obtaining the B.P.N. for the molecule is as follows:

5 carbon atoms in main chain	4.0
10 hydrogen atoms attached to main chain	10.0
2 methyl radicals	6.1
2,2-dimethyl grouping	− 0.4
B.P.N. calculated	19.7

A B.P.N. of 19.7 gives a calculated boiling point of 78.6°, and the observed boiling point of the substance has been recorded as 80.5°.

Boiling Points of Olefins

"The calculation of the boiling point of an olefin follows the same general procedure as that for a paraffin with the exception that a B.P.N. must be included to account for the ethylenic linkage. The value of the latter varies with the degree of substitution, and different B.P.N.'s have been assigned depending upon this factor. The B.P.N.'s for the ethylenic linkages are given in Table 3.6 (page 91). The longest chain in the molecule must always be used in calculating the boiling point, regardless of whether this places the unsaturated linkage in the side chain or not. When there are two chains of equal length, one saturated and the other unsaturated, it has been found desirable to choose the saturated chain as the base. As a consequence of this procedure the $R_2C=CH_2$ type of olefin is considered a methylene derivative of the saturated chain. In explanation, the boiling point of 2-methylene-6-methyloctane may be calculated as follows:

8 carbon atoms in the main chain	6.4
15 hydrogen atoms attached to the main chain	15.0
1 methyl radical	3.05
1 methylene radical	4.4
B.P.N.	28.85

The B.P.N. of 28.85 gives a calculated boiling point of 162.9°C. The observed boiling point is 163.5° C.

"Perhaps the most striking fact brought out by a comparison of the B.P.N.'s of the olefins is that substitution of alkyl radicals on the ethylenic linkage appears to increase rather than to decrease the B.P.N. of the ethylenic linkage. This appears to contradict the rules of steric effects, but probably does not because the effect upon the alkyl groups attached to the double bond would be greater than on the carbon atoms of the double bond which are on the inside of the molecule. It must be remembered that the values of the B.P.N.'s for the alkyl groups were obtained from the parafin hydrocarbons, and to use those values for the alkyl groups attached to ethylenic linkages will not accurately represent the effect upon the boiling point. However, instead of assigning a constant value to the double bond, it is much simpler to use the same values for the alkyl groups in all cases and to assign characteristic values to each type of ethylenic linkage. A similar behavior is observed for the acetylenic hydrocarbons. The number of possible substitutions is much less with the acetylenes, but the disubstituted acetylenic derivatives require a larger B.P.N. than the monosubstituted or acetylene itself. Also the 2-alkynes have higher boiling points and B.P.N.'s than the corresponding 3-, 4-, etc., alkynes. Again, there is correlation between the olefins and the acetylenes, but the exaltation of the 2-alkenes is comparatively small and no account has been made of this difference."

Boiling Point Numbers for the Cis-Trans Isomers

"B.P.N.'s for the *cis-trans* isomers of certain types of olefins should be considered also. It is unfortunate that the boiling points of so few isomers of this kind have been recorded and that so much confusion exists as to whether the *cis* or the *trans* isomer has the higher boiling point, but with the development of efficient fractionating equipment it is hoped that much more reliable information will become available. In 1900 Wislicenus and students suggested that *cis*-2-butene had a lower boiling point than the *trans* isomer. In 1904 Pfeiffer and in 1929 Lucas and co-workers took the opposite view. In 1932 Schmitt and Boord, after studying the properties of a number of the higher olefins, suggested the following: 'If it is true that an isomer having its double bond most deeply buried in the molecular structure has the highest boiling point, then one would expect this to be the *trans* isomer.' The work on boiling point numbers substantiates the view of Schmitt and Boord that the olefin with the most highly substituted double bond has the highest boiling point, but it has also been suggested above that this effect is due to the greater effect on the boiling point of the alkyl groups as compared with the effect of the same groups in the corresponding paraffin, which appears more likely than that the effect is due to the double bond being 'most deeply buried.' Kistiakowsky and collaborators obtained more direct evidence from their work on the heats of hydrogenation of the *cis*- and *trans*-2-butenes, which proves that the *cis* isomer has the higher boiling point, assuming that the *cis* isomer has a higher heat of hydrogenation. Also, evidence has been obtained from x-ray and electron studies which indicates that *cis*-dichloroethylene has the higher boiling point. On the other hand, it appears likely that *cis*-diiodoethylene has a lower boiling point. In view of these conflicting and meager data no attempt has been made to assign B.P.N.'s to the *cis-trans* structural grouping at this time."

Effect of Relative Position of Double Bonds in Diolefins and Triolefins on Boiling Point

"The effect of several unsaturated linkages upon the boiling point depends upon the position of the bonds in respect to one another. The allenes and conjugated polyolefins show a marked effect, and B.P.N.'s representing this behavior must be used to calculate the B.P.N.'s and boiling points of such compounds. Where the unsaturated linkages are separated by two or more single bonds, there is no noticeable effect and the normal values only are used. The B.P.N. of the allenic linkage appears to be constant regardless of its position in the chain or the extent of the alkylation upon it. This is surprising, considering the behavior of the simple olefins and other diolefins as well, but gives satisfactory results with the known allenic hydrocarbons.

"The conjugated diolefins require the additional B.P.N. of 0.8 unit be-

(Text continued on page 86)

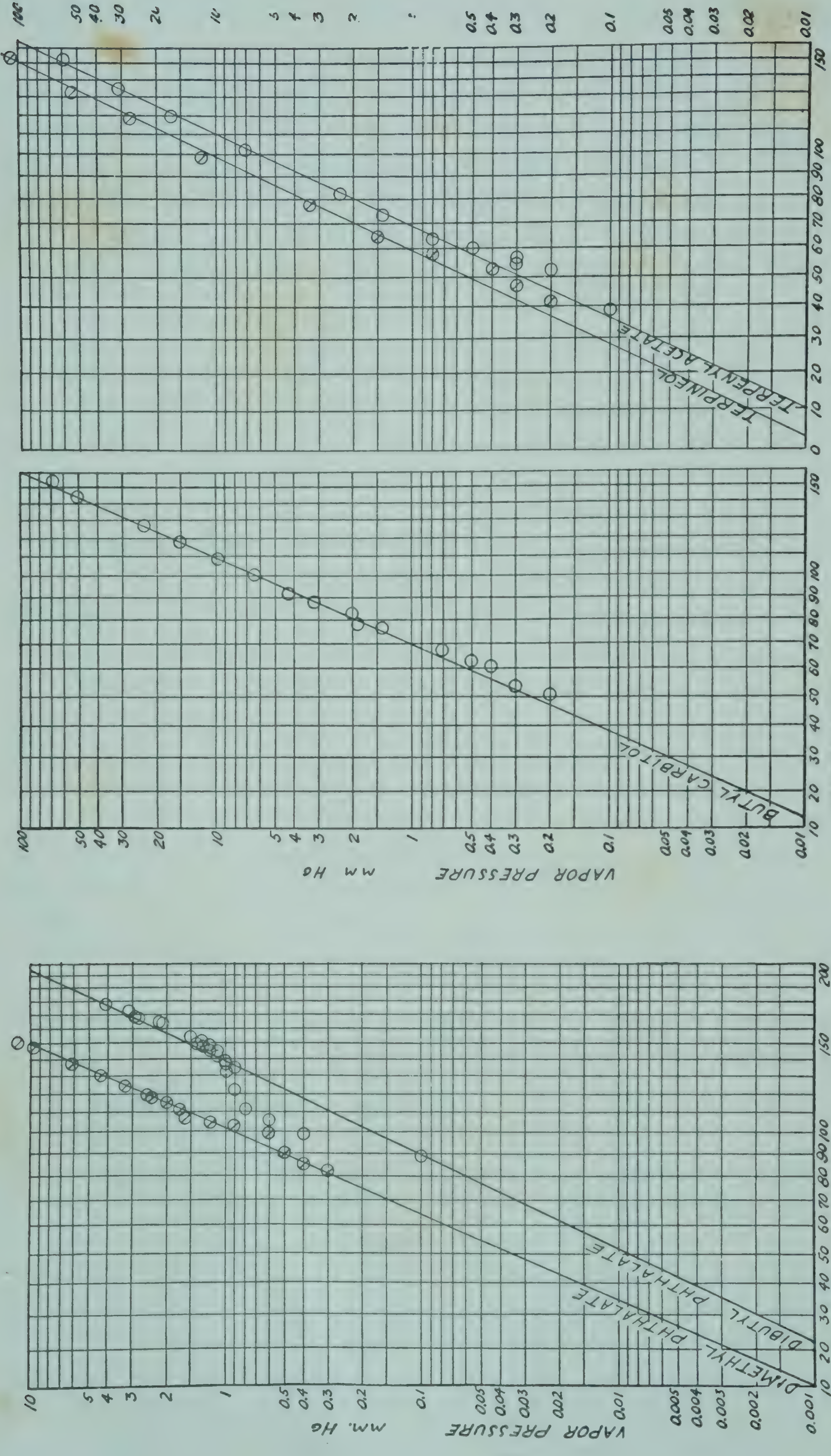


Figure 3.13. Vapor Pressure of Various Solvents at Different Temperatures.[11]

TABLE 3.2. CONSTANT BOILING MIXTURES

First Component	% By Weight	Second Component	% By Weight	Boiling Point (° C.)
Acetone	34.0	Carbon disulfide	66.0	39.25
Acetone	20.0	Chloroform	80.0	64.7
Acetone	38.0	Diethylamine	62.0	51.5
Acetone	97.5	Isoamyl acetate	2.5	131.3
Acetone	64.4	Methyl acetate	35.6	56.1
Acetone	86.5	Methyl alcohol	13.5	55.95
n-Amyl alcohol	94.3	Isoamyl acetate	5.7	131.3
n-Amyl alcohol	77.5	Isoamyl propionate	22.5	130.5
n-Amyl formate	57.0	*n*-Amyl alcohol	43.0	130.4
n-Amyl formate	71.6	Water	28.4	91.6
Benzene	55.0	Cyclohexane	45.0	77.8
Benzene	68.0	Ethyl alcohol	32.0	68.2
Benzene	19.0	*n*-Hexane	81.0	68.9
Benzene	91.0	Isobutyl alcohol	9.0	79.8
Benzene	67.0	Isopropyl alcohol	33.0	71.9
Benzene	60.0	Methyl alcohol	40.0	58.3
Benzene	62.0	Methyl ethyl ketone	38.0	78.3
Benzene	83.0	*n*-Propyl alcohol	17.0	77.1
Bromoform	96.6	Ethyl alcohol	3.4	59.3
Bromoform	97.9	Isopropyl alcohol	2.1	60.8
Bromoform	93.6	Methyl alcohol	6.4	53.5
n-Butyl acetate	54.0	*n*-Butyl alcohol	46.0	118.0
n-Butyl acetate	48.0	Isopropyl alcohol	52.0	80.1
n-Butyl acetate	60.0	*n*-Propyl alcohol	40.0	94.2
n-Butyl acetate	71.3	Water	28.7	90.2
n-Butyl alcohol	44.8	*n*-Butyl acetate	55.2	113.5
n-Butyl alcohol	24.0	*n*-Butyl formate	76.0	105.8
n-Butyl alcohol	63.0	Chlorobenzene	37.0	107.2
n-Butyl alcohol	9.8	Cyclohexane	90.2	79.8
n-Butyl alcohol	19.9	Ethyl isobutyrate	80.1	108.5
n-Butyl alcohol	30.8	Methyl isovalerate	69.2	113.0
n-Butyl alcohol	32.0	Perchlorethylene	68.0	110.0
n-Butyl alcohol	33.5	Tetrachlorethylene	66.5	110.0
n-Butyl alcohol	32.1	Toluene	67.9	105.2
n-Butyl alcohol	62.7	Water	37.3	92.3
sec-Butyl alcohol	55.2	Ethyl propionate	44.8	85.5
sec-Butyl alcohol	52.1	*n*-Propyl acetate	47.9	96.5
tert-Butyl alcohol	32.4	Benzene	67.6	74.0
tert-Butyl alcohol	52.0	Ethylbutyrate	48.0	105.5
tert-Butyl alcohol	7.0	*n*-Methyl butyrate	93.0	100.8
tert-Butyl alcohol	9.0	*n*-Propyl acetate	91.0	101.0
Carbon tetrachloride	88.0	Allyl alcohol	12.0	72.32
Carbon tetrachloride	83.5	*tert*-Butyl alcohol	16.5	69.5
Carbon tetrachloride	56.8	Ethyl acetate	43.2	74.75
Carbon tetrachloride	84.1	Ethyl alcohol	15.9	64.95
Carbon tetrachloride	82.0	Isopropyl alcohol	18.0	67.0
Carbon tetrachloride	79.3	Methyl alcohol	20.7	55.7
Carbon tetrachloride	70.9	Methyl ethyl ketone	29.1	73.8
Carbon tetrachloride	59.7	Methyl propionate	40.3	75.5
Carbon tetrachloride	88.4	*n*-Propyl alcohol	11.6	72.8
"Cellosolve"	40.0	Water	60.0	98–99
Chlorbenzene	37.0	*n*-Butyl alcohol	63.0	107.2
Chlorbenzene	64.0	Isoamyl alcohol	36.0	124.3
Chlorbenzene	20.0	*n*-Propyl alcohol	80.0	96.5
Chloroform	80.0	Acetone	20.0	64.7
Chloroform	93.0	Ethyl alcohol	7.0	59.4
Chloroform	72.0	*n*-Hexane	28.0	60.0
Chloroform	22.0	Methyl acetate	78.0	64.5
Chloroform	87.5	Methyl alcohol	12.5	53.5
Cyclohexane	45.0	Benzene	55.0	77.8

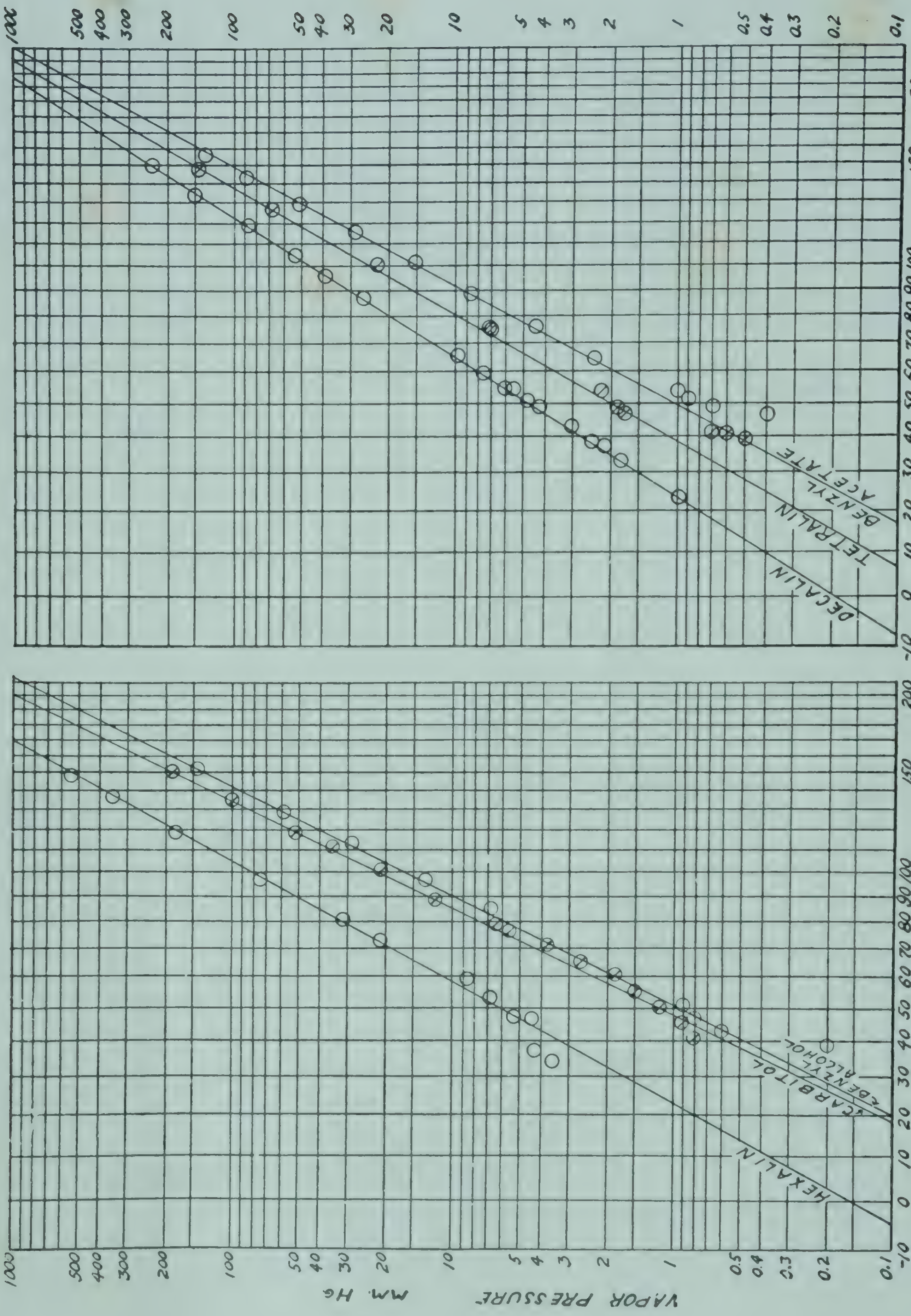


Figure 3.14. Vapor Pressure of Various Solvents at Different Temperatures.[11]

TABLE 3.2. CONSTANT BOILING MIXTURES—*Continued*

First Component	% By Weight	Second Component	% By Weight	Boiling Point (° C.)
Cyclohexane	90.0	*n*-Butyl alcohol	10.0	79.8
Cyclohexane	70.0	Ethyl alcohol	30.0	64.9
Cyclohexane	86.0	Isobutyl alcohol	14.0	78.1
Cyclohexane	67.0	Isopropyl alcohol	33.0	68.6
Cyclohexane	63.0	Methyl alcohol	37.0	54.2
Cyclohexane	80.0	*n*-Propyl alcohol	20.0	74.3
Cyclohexanol	41.0	Camphene	59.0	152.0
Cyclohexanol	70.2	Cymene	29.8	159.0
Cyclohexanol	45.0	Furfural	55.0	156.0
Cyclohexanol	18.5	Isoamyl butyrate	81.5	155.0
Cyclohexanol	69.9	Isoamyl propionate	30.1	157.7
Cyclohexanol	36.0	Pentachloroethane	64.0	158.0
Cyclohexanol	35.0	Pinene	65.0	150.0
Cyclohexanol	5.2	*m*-Xylene	94.8	138.9
Cyclohexanone	56.0	Camphor	44.0	151.0
Cyclohexanone	55.0	Tetrachloroethane	45.0	159.0
Cyclohexanone	39.0	Trichlorhydrin	61.0	160.0
Dichlorobromomethane	59.6	Ethyl alcohol	40.4	75.5
Dichlorobromomethane	81.8	Isobutyl alcohol	18.2	89.3
Dichlorobromomethane	50.9	Isopropyl alcohol	49.1	78.0
Dichlorobromomethane	70.1	*n*-Propyl alcohol	29.9	86.4
1,1-Dichloroethane	91.8	Ethyl alcohol	8.2	54.5
Dichlorethylene	82.5	*n*-Propyl alcohol	17.5	80.0
Dimethyl carbonate	77.7	*n*-Propyl alcohol	22.3	88.2
Dimethyl ketone	25.9	*tert*-Amyl ketone	74.1	98.5
Dioxane	2.5	Isoamyl alcohol	97.5	131.3
Dioxane	80.0	Water	20.0	86.8
Dioxane	40.0	*m*-Xylene	60.0	136.0
Epichlorhydrin	30.0	*tert*-Amyl alcohol	70.0	100.1
Epichlorhydrin	57.0	*n*-Butyl alcohol	43.0	112.0
Epichlorhydrin	80.9	Isoamyl alcohol	19.1	115.4
Epichlorhydrin	39.4	Isobutyl alcohol	60.6	105.0
Epichlorhydrin	21.7	*n*-Propyl alcohol	78.3	98.8
Epichlorhydrin	52.0	Tetrachloroethylene	48.0	110.0
Epichlorhydrin	26.1	Toluene	73.9	108.3
Ethanol	32.0	Benzene	68.0	68.2
Ethanol	9.0	Carbon disulfide	91.0	42.4
Ethanol	15.8	Carbon tetrachloride	84.2	64.9
Ethanol	7.0	Chloroform	93.0	59.4
Ethanol	30.5	Cyclohexane	69.5	64.9
Ethanol	31.0	Ethyl acetate	69.0	71.8
Ethanol	3.1	Ethyl bromide	96.9	37.6
Ethanol	48.0	*n*-Heptane	52.0	72.0
Ethanol	21.0	*n*-Hexane	79.0	58.6
Ethanol	34.0	Methyl ethyl ketone	66.0	74.8
Ethanol	52.0	Methyl propionate	48.0	93.2
Ethanol	81.0	Perchlorethylene	19.0	78.0
Ethanol	57.3	*n*-Propyl formate	42.7	73.5
Ethanol	81.0	Tetrachlorethylene	19.0	78.0
Ethanol	68.0	Toluene	32.0	76.6
Ethanol	27.0	Trichlorethylene	73.0	70.9
Ethanol	95.6	Water	4.4	78.2
Ethyl acetate	74.0	*tert*-Butanol	26.0	75.2
Ethyl acetate	3.0	Carbon disulfide	97.0	46.1
Ethyl acetate	43.1	Carbon tetrachloride	56.9	74.8
Ethyl acetate	69.2	Ethanol	30.8	71.8
Ethyl acetate	77.0	Isopropanol	23.0	74.8
Ethyl acetate	20.0	Methanol	80.0	62.3
Ethyl acetate	93.9	Water	6.1	70.4
Ethyl ether	99.0	Carbon disulfide	1.0	34.5

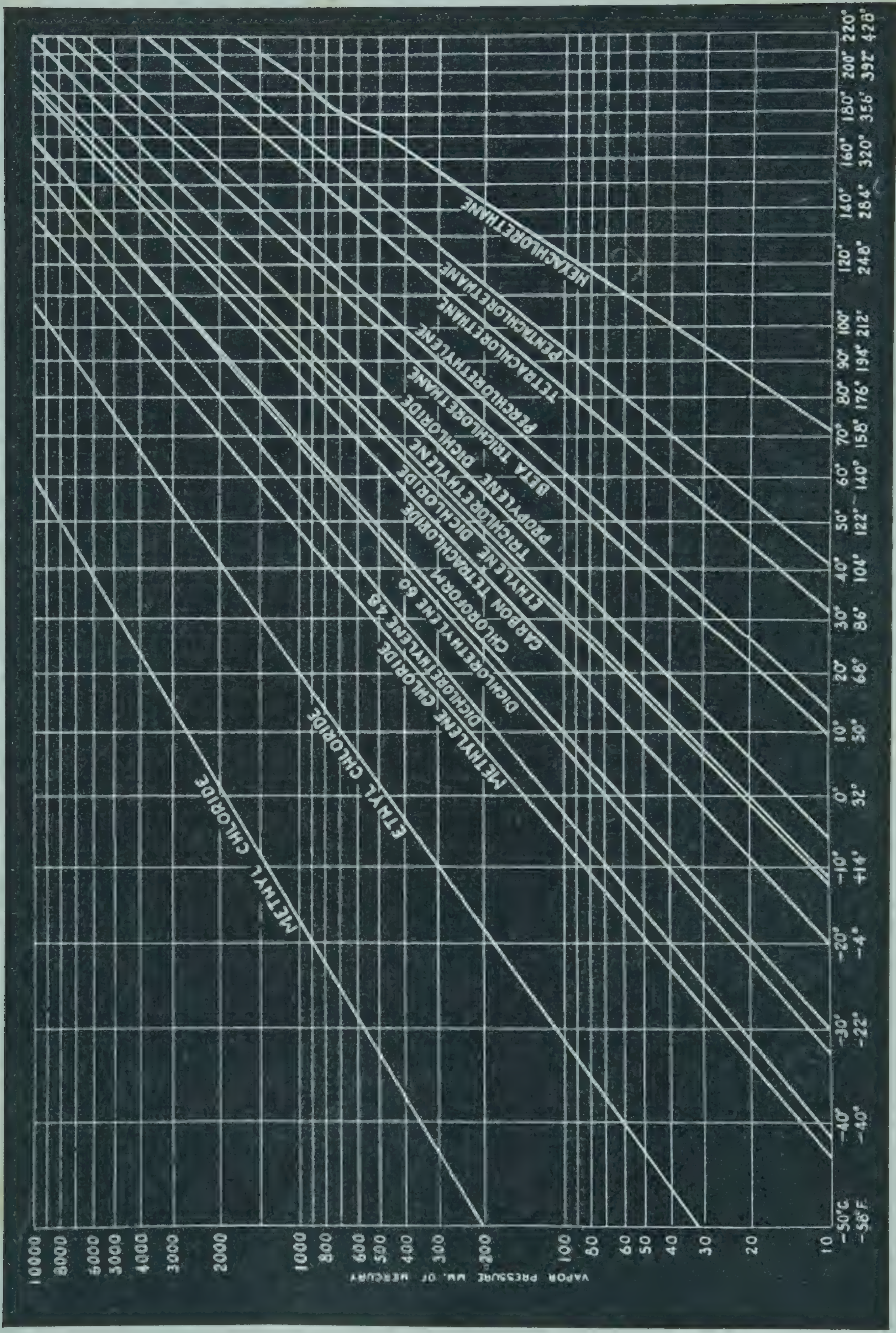


Figure. 3.15. Vapor Pressures.

TABLE 3.2. CONSTANT BOILING MIXTURES—*Continued*

First Component	% By Weight	Second Component	% By Weight	Boiling Point (° C.)
Ethyl ether	44.5	Methyl formate	55.5	28.2
Ethyl ether	98.9	Water	1.1	34.1
Ethyl formate	37.0	Carbon disulfide	63.0	39.4
Ethyl formate	84.0	Methyl alcohol	16.0	51.0
Ethylene bromide	44.9	Acetic acid	55.1	114.35
Ethylene bromide	89.9	Ethylbenzene	10.1	131.1
Ethylene bromide	10.1	Isoamyl alcohol	89.9	123.2
Ethylene bromide	41.7	Isobutyl alcohol	58.3	106.2
Ethylene bromide	82.4	Propionic acid	17.6	127.75
Ethylene chlorhydrin	42.0	Water	58.0	96.0
Furfural	40.0	Camphene	60.0	147.0
Furfural	55.0	Cyclohexanol	45.0	156.0
Furfural	38.0	Pinene	62.0	143.0
Isoamyl acetate	50.0	*m*-Xylene	50.0	136.0
Isoamyl alcohol	36.0	Chlorobenzene	64.0	124.3
Isoamyl alcohol	19.0	Epichlorhydrin	81.0	115.4
Isoamyl alcohol	97.5	Isoamyl acetate	2.5	131.3
Isoamyl alcohol	26.0	Isoamyl formate	74.0	123.6
Isoamyl alcohol	19.0	Tetrachlorethylene	81.0	116.0
Isoamyl alcohol	49.3	Ethylbenzene	50.7	125.9
Isoamyl alcohol	53.4	*m*-Xylene	46.6	127.0
Isoamyl alcohol	59.6	*o*-Xylene	40.4	128.0
Isoamyl alcohol	51.3	*p*-Xylene	48.7	126.0
Isoamyl formate	74.0	Isoamyl alcohol	26.0	123.6
Isoamyl formate	79.0	Water	21.0	90.2
Isobutyl acetate	53.0	*n*-Butyl alcohol	47.0	117.2
Isobutyl acetate	55.0	Isobutyl alcohol	45.0	107.4
Isobutyl acetate	71.0	Water	29.0	90.3
Isobutyl alcohol	9.5	Benzene	90.5	79.84
Isobutyl alcohol	14.0	Cyclohexane	86.0	78.1
Isobutyl alcohol	44.5	Toluene	55.5	101.15
Isobutyl alcohol	67.0	Water	33.0	90.0
Isopropyl acetate	47.7	Isopropanol	52.3	80.1
Isopropyl acetate	90.0	Water	10.0	75.0
Isopropyl alcohol	55.0	Acetonitrile	45.0	75.0
Isopropyl alcohol	32.4	Benzene	67.6	71.9
Isopropyl alcohol	8.1	Carbon disulfide	91.9	44.6
Isopropyl alcohol	18.0	Carbon tetrachloride	82.0	67.0
Isopropyl alcohol	4.2	Chloroform	95.8	60.8
Isopropyl alcohol	66.5	Chlorpicrin	33.5	82.0
Isopropyl alcohol	36.0	1-3 Cyclohexadiene	64.0	70.4
Isopropyl alcohol	32.8	Cyclohexane	67.2	68.6
Isopropyl alcohol	36.0	Cyclohexene	64.0	71.0
Isopropyl alcohol	27.6	Dichlorbromomethane	72.4	78.0
Isopropyl alcohol	22.9	Ethyl acetate	77.1	74.8
Isopropyl alcohol	45.0	Ethylene dichloride	55.0	74.0
Isopropyl alcohol	22.2	*n*-Hexane	77.8	61.0
Isopropyl alcohol	33.0	Isobutyl bromide	67.0	75.5
Isopropyl alcohol	17.1	Isobutyl chloride	82.9	63.8
Isopropyl alcohol	76.5	Isobutyl iodide	23.5	81.8
Isopropyl alcohol	52.3	Isopropyl acetate	47.7	80.1
Isopropyl alcohol	10.0	Isopropyl ether	90.0	64.9
Isopropyl alcohol	30.0	Methyl ethyl ketone	70.0	77.3
Isopropyl alcohol	3.1	Methyl iodide	96.9	42.3
Isopropyl alcohol	28.2	Methyl propionate	71.8	77.0
Isopropyl alcohol	16.0	*n*-Propyl bromide	84.0	65.2
Isopropyl alcohol	3.9	*n*-Propyl chloride	96.1	45.8
Isopropyl alcohol	80.6	Tetrachlorethylene	19.4	81.7
Isopropyl alcohol	68.6	Toluene	31.4	80.6
Isopropyl alcohol	28.0	Trichlorethylene	72.0	74.0

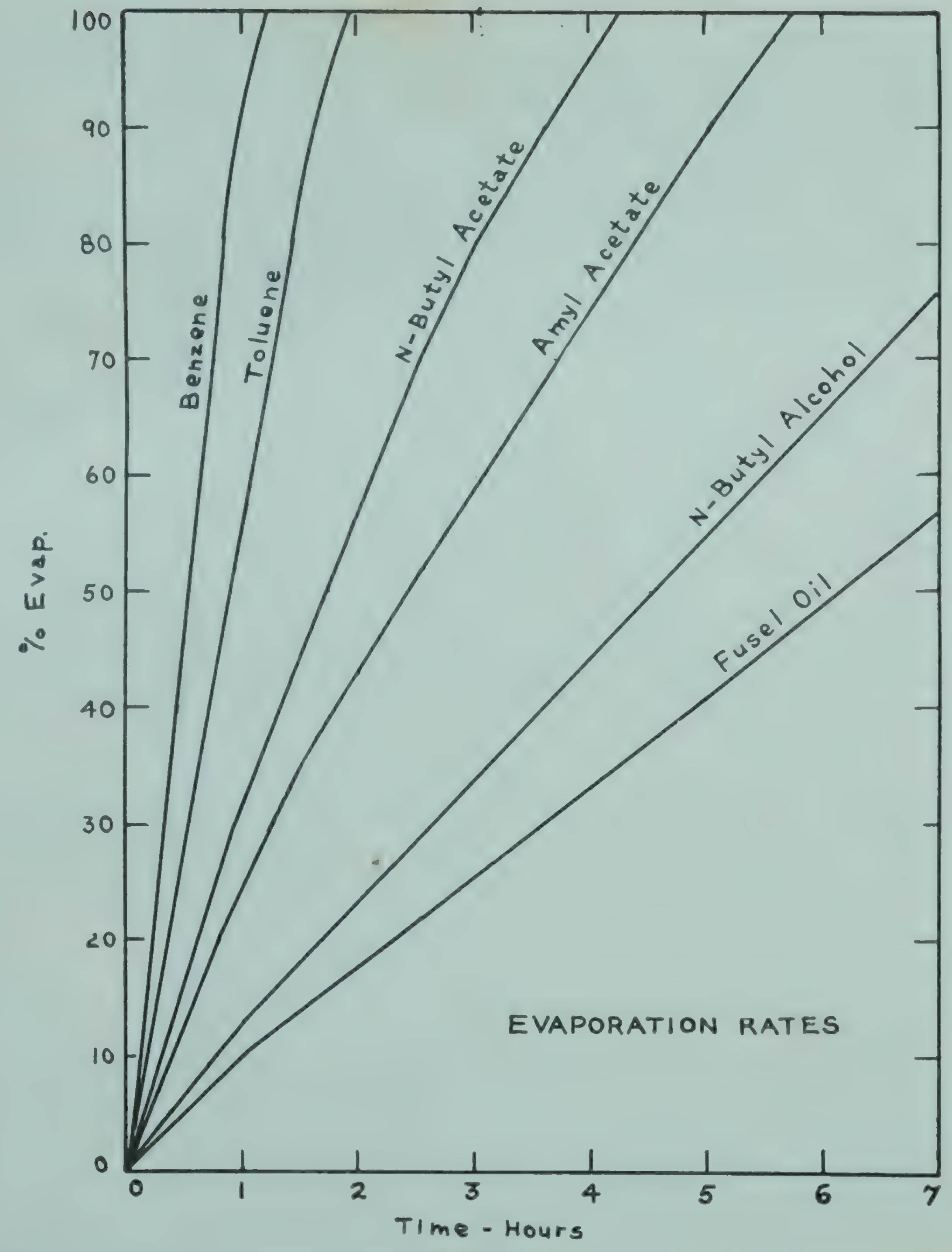


Figure 3.16. Evaporation Rate of Various Solvents at Room Temperature.[2]

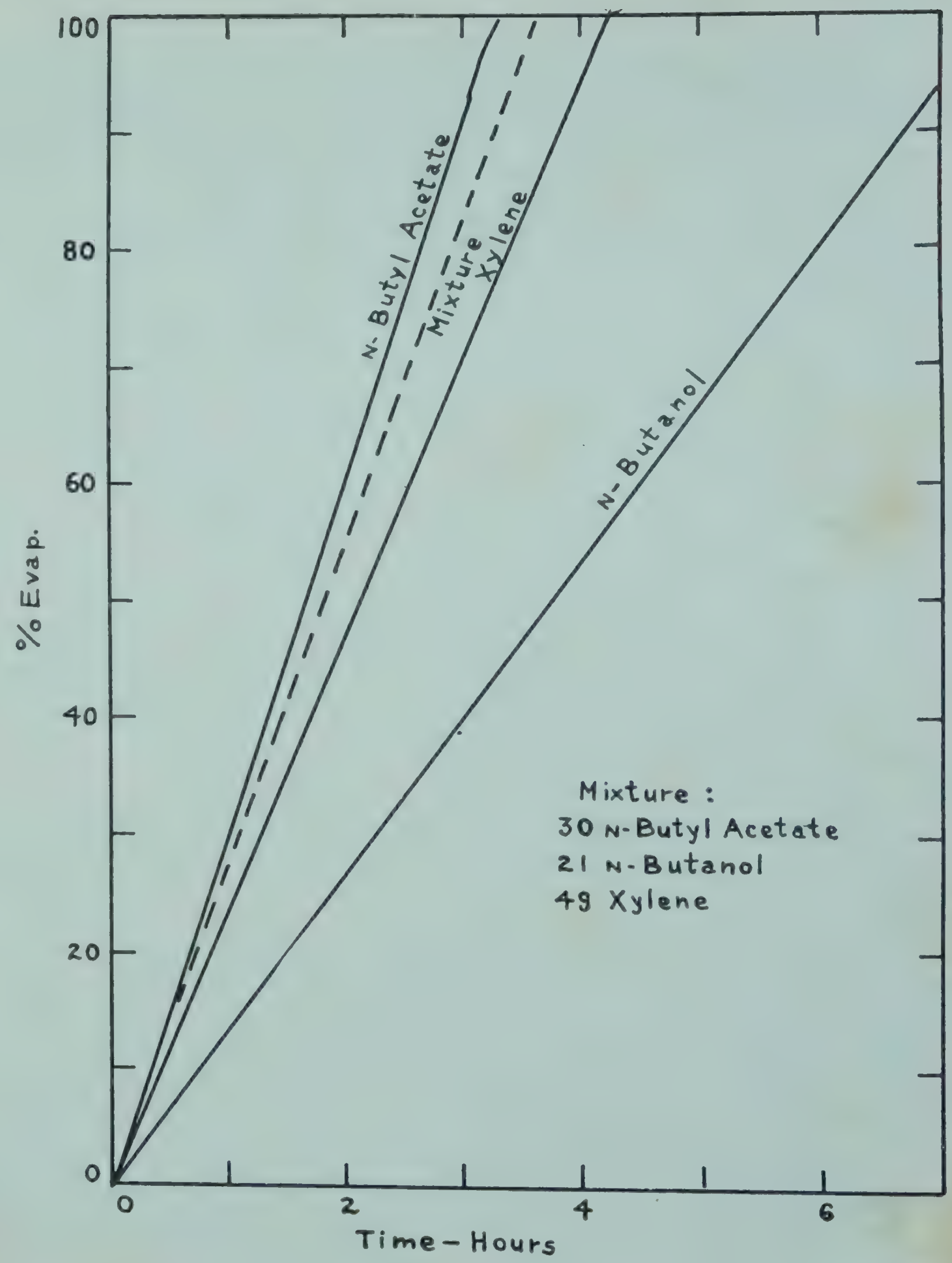


Figure 3.17. Evaporation Rate of Various Solvents at Room Temperature.[2]

TABLE 3.2. CONSTANT BOILING MIXTURES—*Continued*

First Component	% By Weight	Second Component	% By Weight	Boiling Point (° C.)
Isopropyl alcohol	87.7	Water	12.3	80.4
Isopropyl ether	20.0	Acetone	80.0	53.6
Isopropyl ether	70.0	Chloroform	30.0	68.5-69.5
Isopropyl ether	85–90	Ethyl alcohol	10–15	63.0
Isopropyl ether	90.0	Isopropanol	10.0	64.8-64.9
Methyl acetate	45.0	Acetone	55.0	56.1
Methyl acetate	30.0	Carbon disulfide	70.0	40.2
Methyl acetate	30.0	Isopropyl alcohol	70.0	77.3
Methyl acetate	81.0	Methyl alcohol	19.0	54.0
Methyl alcohol	15.0	Acetone	85.0	55.9
Methyl alcohol	40.0	Benzene	60.0	58.3
Methyl alcohol	20.0	Carbon disulfide	80.0	37.6
Methyl alcohol	37.0	Carbon tetrachloride	63.0	54.2
Methyl alcohol	20.0	Chloroform	80.0	64.7
Methyl alcohol	37.0	Cyclohexane	63.0	54.2
Methyl alcohol	11.4	1,1-Dichloroethane	88.6	49.05
Methyl alcohol	80.0	Ethyl acetate	20.0	62.3
Methyl alcohol	16.0	Ethyl formate	84.0	51.0
Methyl alcohol	62.0	*n*-Heptane	38.0	60.5
Methyl alcohol	27.0	*n*-Hexane	73.0	50.0
Methyl alcohol	19.0	Methyl acetate	81.0	54.0
Methyl alcohol	70.5	Methylcyclohexane	29.5	60.0
Methyl alcohol	91.8	*n*-Propyl formate	8.2	63.7
Methyl alcohol	36.0	Trichlorethylene	64.0	60.2
Methyl alcohol	67.3	Trimethyl borate	32.7	59.0
Methyl ethyl ketone	37.5	Benzene	62.5	78.4
Methyl ethyl ketone	34.0	Carbon disulfide	66.0	39.2
Methyl ethyl ketone	29.0	Carbon tetrachloride	71.0	73.8
Methyl ethyl ketone	40.0	Ethyl alcohol	60.0	74.8
Methyl ethyl ketone	26.0	Isoamyl formate	74.0	123.6
Methyl ethyl ketone	30.0	Isopropyl alcohol	70.0	77.3
Methyl ethyl ketone	86.0	Methyl alcohol	14.0	55.9
Methyl ethyl ketone	52.0	Methyl propionate	48.0	79.25
Methyl ethyl ketone	55.0	Propyl formate	45.0	79.45
Methyl ethyl ketone	88.6	Water	11.4	73.6
Methyl formate	64.1	Ethyl bromide	35.9	29.9
Methyl formate	56.4	Ethyl ether	43.6	28.3
Methyl propyl ketone	39.0	Methyl cyclohexane	61.0	100.6
Methyl propyl ketone	36.5	*n*-Propyl acetate	63.5	101.35
Pentachlorethane	85.0	Clycol	15.0	154.5
Perchlorethylene	48.0	α-Epichlorhydrin	52.0	110.0
Perchlorethylene	19.0	Ethyl alcohol	81.0	78.0
Perchlorethylene	81.0	Isoamyl alcohol	19.0	116.0
Perchlorethylene	60.0	Isobutyl alcohol	40.0	103.0
Perchlorethylene	46.0	*n*-Propyl alcohol	54.0	94.0
n-Propyl acetate	66.8	*tert*-Amyl alcohol	33.2	98.5
n-Propyl acetate	43.0	Carbon tetrachloride	57.0	74.7
n-Propyl acetate	77.0	Isopropyl alcohol	23.0	74.8
n-Propyl acetate	60.0	*n*-Propyl alcohol	50.0	94.2
n-Propyl acetate	86.0	Water	14.0	82.4
n-Propyl alcohol	16.9	Benzene	83.1	77.12
n-Propyl alcohol	11.5	Carbon tetrachloride	88.5	72.8
n-Propyl alcohol	20.0	Cyclohexane	80.0	74.3
n-Propyl alcohol	57.0	Diethyl ketone	43.0	94.9
n-Propyl alcohol	54.0	Tetrachlorethylene	46.0	94.0
n-Propyl alcohol	51.1	Ethyl propionate	48.9	93.4
n-Propyl alcohol	4.0	*n*-Hexane	96.0	65.6
n-Propyl alcohol	71.1	Methyl butyrate	28.9	94.2

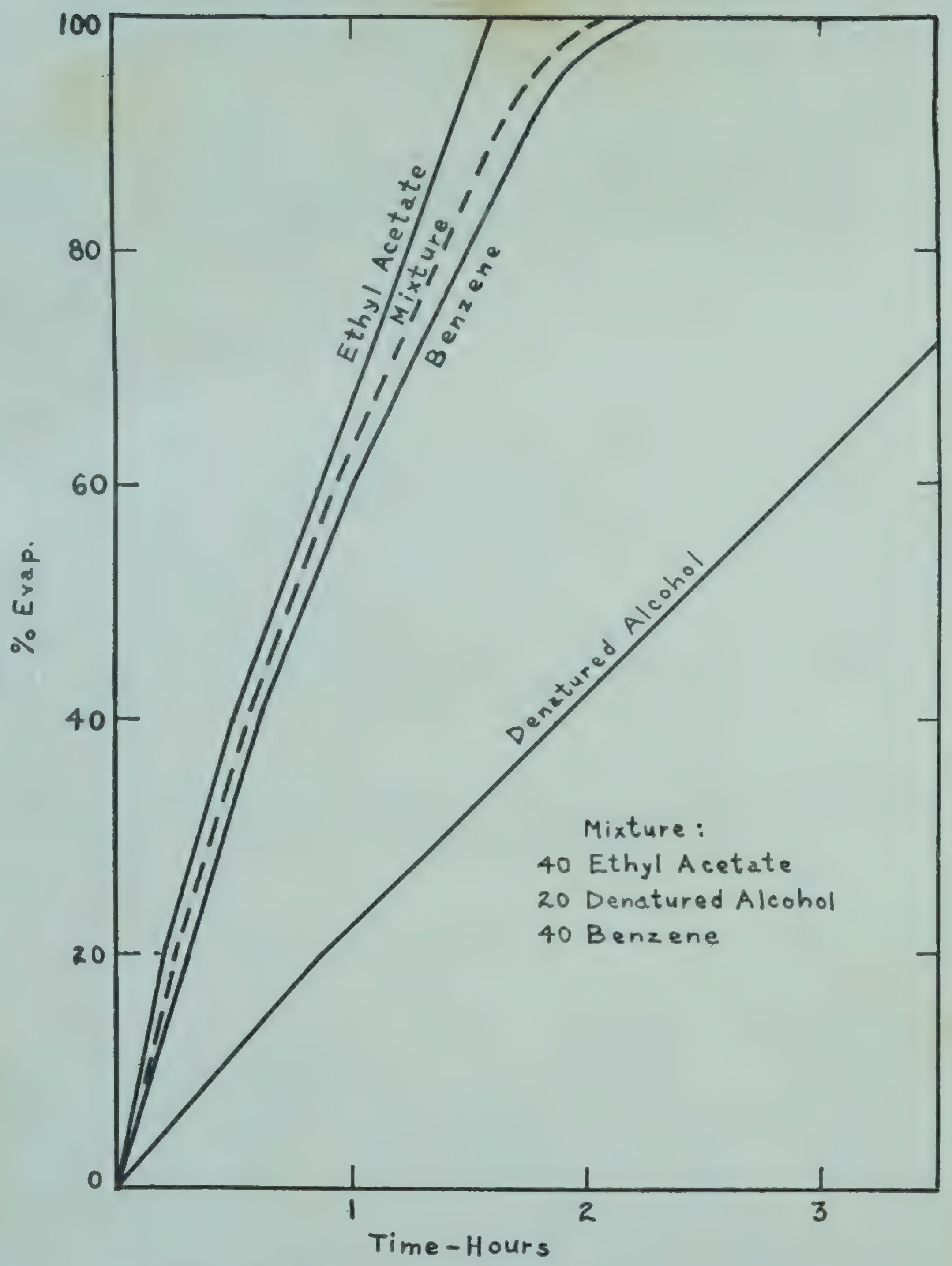


Figure 3.18. Evaporation Rate of Various Solvents at Room Temperature.[2]

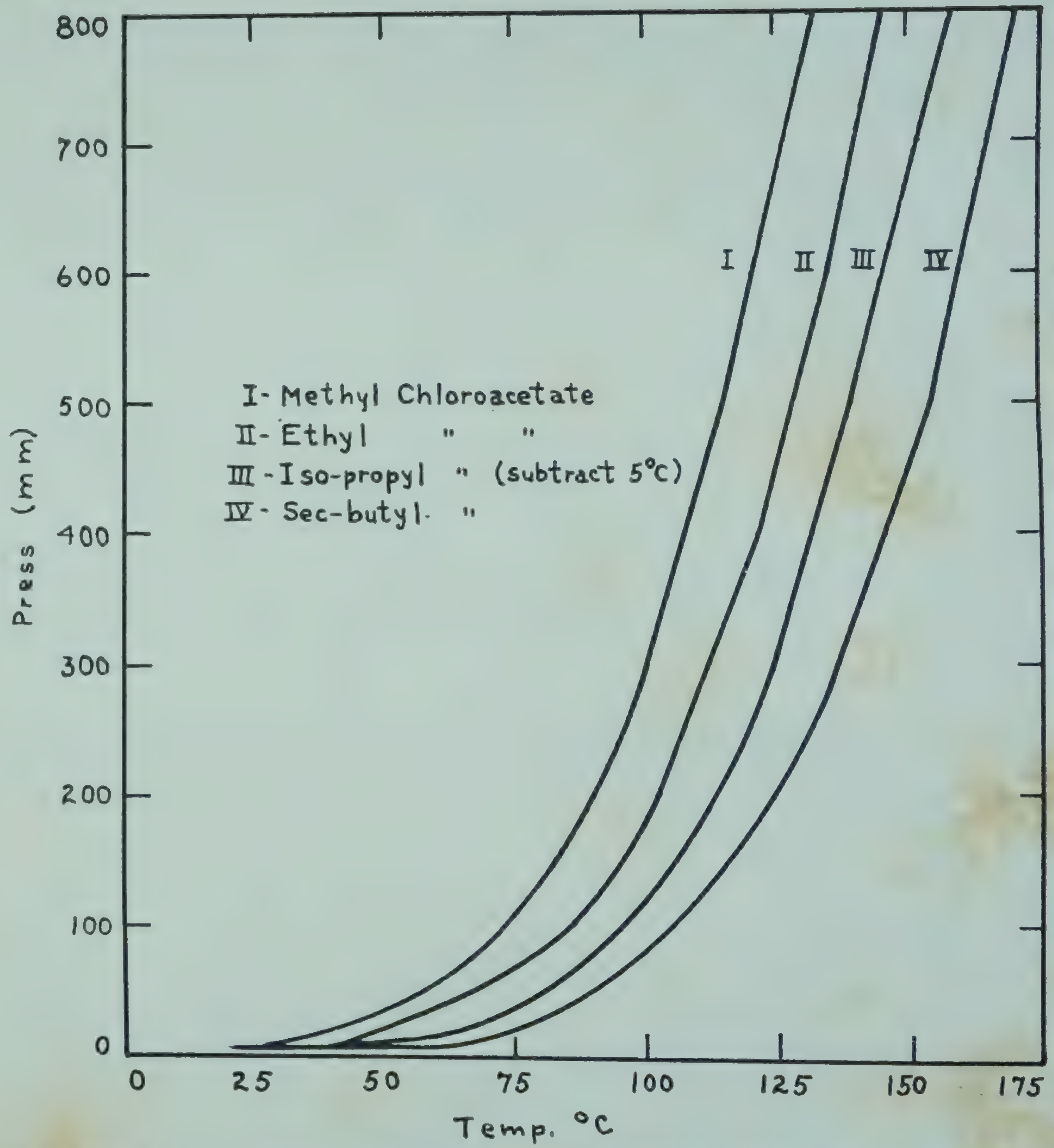


Figure 3.19. Evaporation Rate of Various Solvents at Different Temperatures.[9]

TABLE 3.2. CONSTANT BOILING MIXTURES—*Continued*

First Component	% By Weight	Second Component	% By Weight	Boiling Point (° C.)
n-Propyl alcohol	24.8	Methyl isobutyrate	75.2	89.3
n-Propyl alcohol	80.0	Monochlorbenzene	20.0	96.5
n-Propyl alcohol	74.0	*n*-Octane	26.0	95.0
n-Propyl alcohol	54.0	Perchlorethylene	46.0	94.0
n-Propyl alcohol	62.6	*n*-Propyl acetate	37.4	94.0
n-Propyl alcohol	9.8	*n*-Propyl formate	90.2	80.6
n-Propyl alcohol	77.4	Toluene	22.6	95.0
n-Propyl alcohol	71.7	Water	28.3	87.7
n-Propyl formate	48.0	Benzene	52.0	72.0
Tetrachlorethane	45.0	Cyclohexanone	55.0	159.0
Tetrachlorethane	91.0	Glycol	9.0	145.0
Tetrachlorethane	68.0	Isoamyl acetate	32.0	150.0
Tetrachlorethylene	66.5	*n*-Butyl alcohol	33.5	110.0
Tetrachlorethylene	74.0	Diethyl carbonate	26.0	118.55
Tetrachlorethylene	18.7	Ethyl alcohol	81.3	77.95
Tetrachlorethylene	80.7	Isoamyl alcohol	19.3	116.0
Tetrachlorethylene	59.8	Isobutyl alcohol	40.2	103.05
Tetrachlorethylene	19.3	Isopropyl alcohol	80.7	81.7
Tetrachlorethylene	46.5	*n*-Propyl alcohol	53.5	94.0
Toluene	68.0	*n*-Butyl alcohol	32.0	105.5
Toluene	74.0	Epichlorhydrin	26.0	108.3
Toluene	32.0	Ethyl alcohol	68.0	76.7
Toluene	56.0	Isobutyl alchol	44.0	101.1
Toluene	31.0	Isopropyl alcohol	69.0	80.6
Toluene	51.0	*n*-Propyl alcohol	49.0	92.6
Trichlorethylene	84.0	Allyl alcohol	16.0	80.9
Trichlorethylene	88.0	*tert*-Amyl alcohol	12.0	84.0
Trichlorethylene	86.0	*tert*-Butyl alcohol	14.0	75.0
Trichlorethylene	73.0	Ethyl alcohol	27.0	70.9
Trichlorethylene	92.0	Isobutyl alcohol	8.0	85.4
Trichlorethylene	73.0	Isopropanol	27.0	74.0
Trichlorethylene	64.0	Methanol	36.0	60.2
Trichlorethylene	83.0	*n*-Propyl alcohol	17.0	81.7
Trichlorethylene	93.0	Water	7.0	71.8
1,1,2-Trichlorethylene	35.2	Ethyl alcohol	64.8	77.3
Water	37.3	*n*-Butyl alcohol	62.7	92.25
Water	32.0	*sec*-Butyl alcohol	68.0	88.5
Water	11.7	*tert*-Butyl alcohol	88.3	79.91
Water	6.1	Ethyl acetate	93.9	70.4
Water	4.4	Ethyl alcohol	95.6	78.2
Water	1.3	Ethyl ether	98.7	34.15
Water	27.6	Isoamyl alcohol	72.4	87.0
Water	33.1	Isobutyl alcohol	66.9	89.92
Water	12.3	Isopropyl alcohol	77.8	80.37
Water	10.9	Methyl ethyl ketone	89.1	73.45
Water	28.3	*n*-Propyl alcohol	71.7	87.72
m-Xylene	46.0	Isoamyl acetate	54.0	136.0
m-Xylene	47.0	Isoamyl alcohol	53.0	127.0
o-Xylene	40.0	Isoamyl alcohol	60.0	128.0
p-Xylene	49.0	Isoamyl alcohol	51.0	126.8

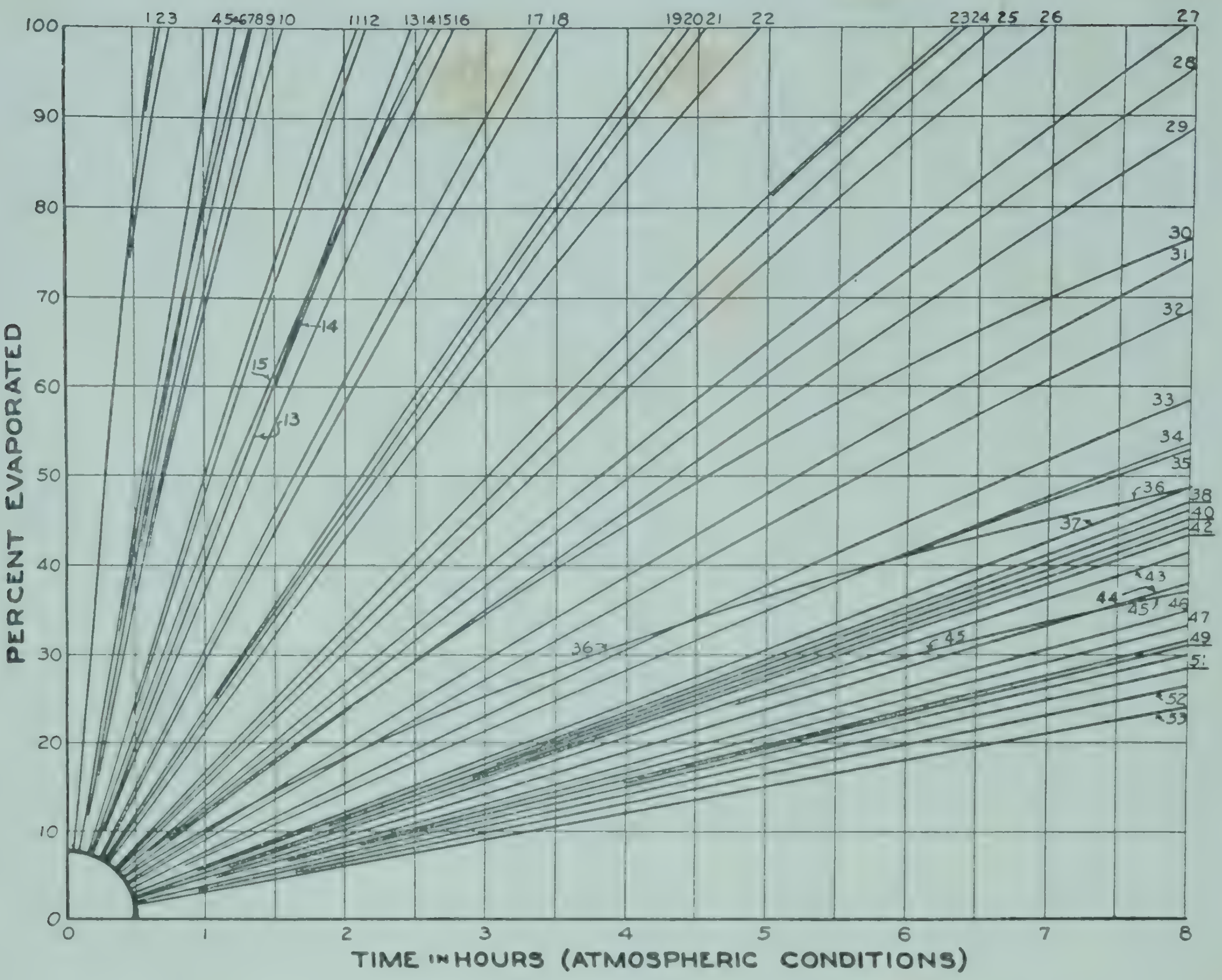


Figure 3.20. Relative Evaporation Rates of Fast to Intermediate Evaporating Liquids at Room Temperature.[10]

1.	Methyl acetate	82%
2.	Acetone	99
3.	Methylacetone (acetone 48 per cent, methyl acetate 28 per cent, methanol, 24%)	—
4.	Cyclohexane	—
5.	Benzene	—
6.	Ethylene dichloride	99
7.	Ethyl acetate	85
8.	Methanol (anhydrous)	99
9.	Methyl ethyl ketone	99
10.	Isopropyl acetate	95
11.	Ethyl propionate	96
12.	Ethanol (anhydrous)	99
13.	Methyl propyl ketone	99
14.	Isopropanol (anhydrous)	99
15.	Diethyl ketone	99
16.	Petroleum nephtha	—
17.	Toluene	—
18.	Solvesso No. 1	—
19.	*sec*-Butyl acetate	82
20.	Hexone (methyl isobutyl ketone)	99
21.	Isobutyl acetate	96
22.	Ethyl butyrate	99
23·	Diethyl "Cellosolve"	95
24.	Diethyl carbonate	91
25.	*sec*-Butanol	99
26.	Monochlorobenzene	99%
27.	*n*-Butyl acetate	90
28.	Mesityl oxide	86
29.	Methyl *n*-butyl ketone	87
30.	Xylene	—
31.	Isobutanol	99
32.	*sec*-Amyl acetate	92
33.	*sec*-Hexyl acetate	98
34.	Amyl acetate, mixed isomers	84
35.	*n*-Butyl propionate	99
36.	Hi-Flash nephtha	—
37.	Methyl "Cellosolve"	99
38.	Dipropyl ketone	99
39·	Methyl amyl acetate	95
40.	Steam-distilled turpentine	—
41.	*n*-Butanol	99
42.	*sec*-Amyl alcohol	99
43.	Gum spirits of turpentine	—
44	Methyl *n*-amyl ketone	98
45.	Solvesso No. 2	—
46.	Amyl alcohol, mixed isomers	99
47.	Methyl amyl alcohol	99
48.	"Cellosolve"	99
49.	Methyl "Cellosolve" acetate	99
50.	Cyclohexanone	67
51.	Isopropyl "Cellosolve"	97
52.	Hexyl (2-ethyl butyl) acetate	91
53.	"Cellosolve" acetate	96

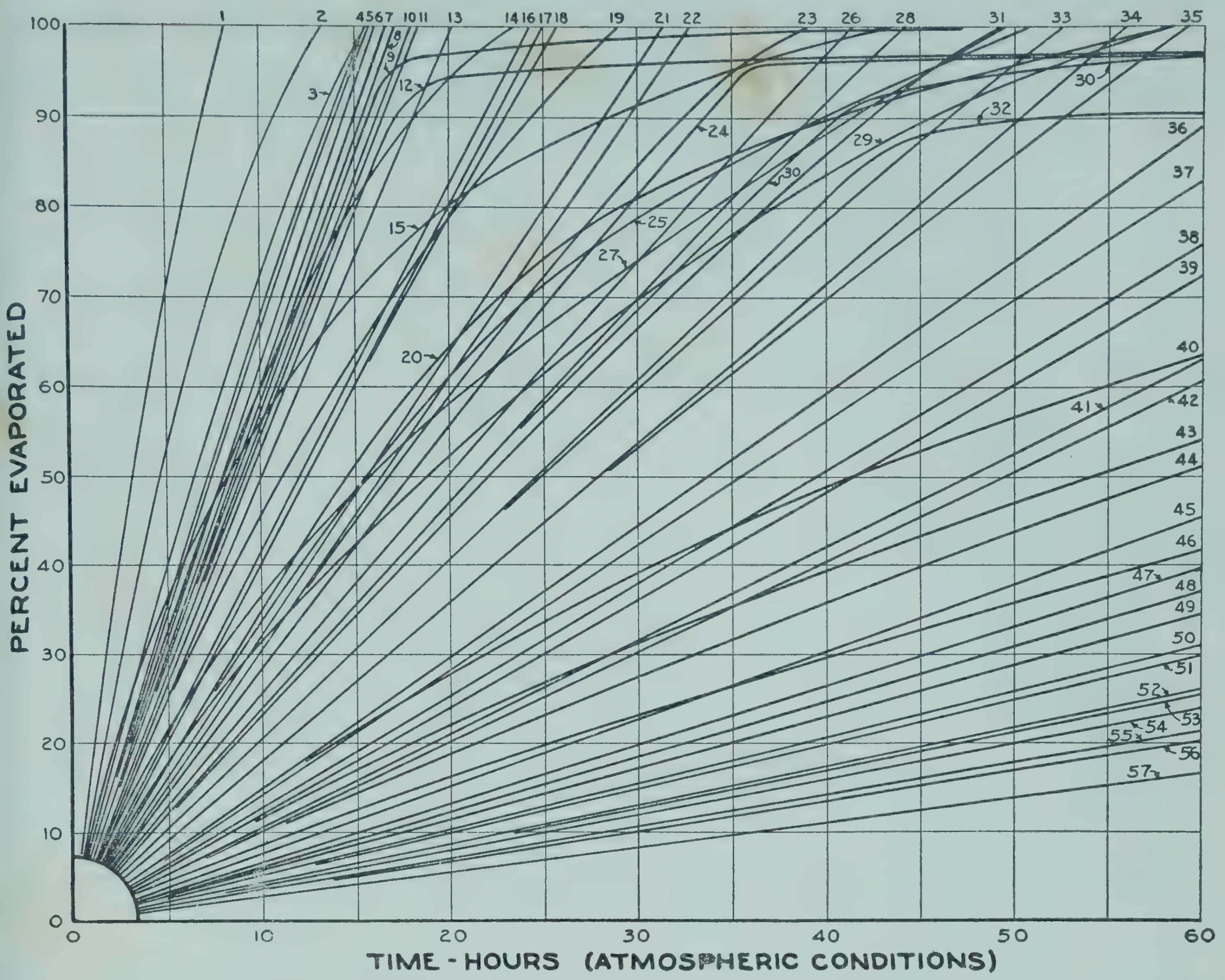


Figure 3.21. Relative Evaporation Rates of Intermediate to Slow Evaporating Liquids.[10]

1. *n*-Butyl acetate	90%	30. Isopropyl lactate	99%
2. Xylene	—	31. Furfural	98
3. *sec*-Hexyl acetate	98	32. Dipentene	—
4. Amyl acetate (mixed isomers)	84	33. *o*-Dichlorobenzene	—
5. *n*-Butyl propionate	99	34. Diacetone alcohol	99
6. Methyl "Cellosolve"	99	35. 3-Methoxy butyl acetate	99
7. Dipropyl ketone	99	36. Methyl *n*-hexyl ketone	96
8. Methyl amyl acetate	95	37. Dichloroethyl ether	99
9. Steam-distilled turpentine	—	38. Decahydronaphthalene	—
10. *n*-Butanol	99	39. Cyclohexanyl acetate	79
11. *sec*-Amyl alcohol	99	40. Hercosol	—
12. Gum spirits of turpentine	—	41. Hexyl (2-ethyl butyl) alcohol)	99
13. Methyl *n*-amyl ketone	98	42. Fenchone	—
14. Amyl alcohol (mixed isomers)	99	43. Safe-T-Esso	—
15. Hi-Flash naphtha	—	44. Phorone	—
16. Methyl amyl alcohol	99	45. Butyl "Cellosolve"	99
17. "Cellosolve"	99	46. Solvesso No. 3	—
18. Methyl "Cellosolve" acetate	99	47. Cyclohexanol	94
19. Solvesso No. 2	—	48. Furfuryl acetate	99
20. Cyclohexanone	67	49. Acetonylacetone	95
21. Isopropyl "Cellosolve"	97	50. Tetrahydrofurfuryl alcohol	99
22. Hexyl (2-ethyl butyl) acetate	91	51. Diethyl "Carbitol"	99
23. "Cellosolve" acetate	96	52. Furfuryl alcohol	98
24. Ethyl lactate	98	53. Tetrahydronaphthalene	—
25. Methylcyclohexanone	74	54. Octyl (2-ethyl hexyl) acetate	99
26. Butyl butyrate	99	55. Butyl "Cellosolve" acetate	99
27. V. M. & P. naphtha	—	56. Butyl lactate	97
28. Diisobutyl ketone	95	57. Glycol diacetate	99
29. Mineral spirits	—		

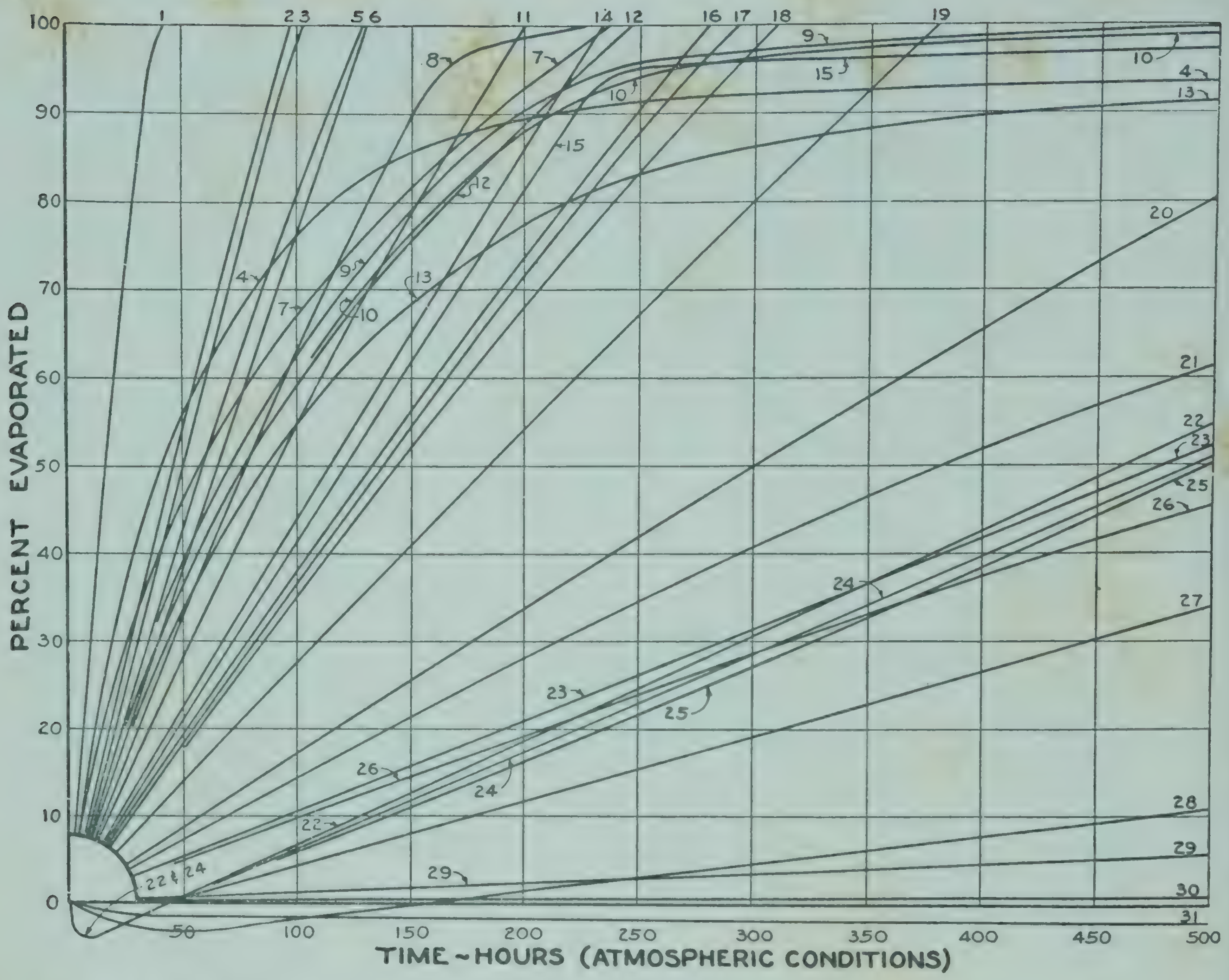


Figure 3.22. Relative Evaporation Rates of Slow to Very Slow Evaporating Liquids at Room Temperature.[10]

1.	"Cellosolve" acetate	96%
2.	Hexyl (2-ethyl butyl) acetate	99
3.	Fenchone	—
4.	Hercosol	—
5.	Phorone	—
6.	Butyl "Cellosolve"	99
7.	Safe-T-Esso	—
8.	Cyclohexanol	94
9.	Furfuryl acetate	99
10.	Tetrahydrofurfuryl alcohol	99
11.	Acetonylacetone	95
12.	Solvesso No. 3	—
13.	Furfuryl alcohol	98
14.	Diethyl "Carbitol"	99
15.	Tetrahydronaphthalene	—
16.	Octyl (2-ethyl hexyl) acetate	99%
17.	Butyl "Cellosolve" acetate	99
18.	Butyl lactate	97
19.	Glycol diacetate	99
20.	Octyl (2-ethyl hexyl) alcohol	99
21.	Pine oil	—
22.	Methyl "Carbitol"	—
23.	Methyl "Carbitol" acetate	99
24.	"Carbitol"	—
25.	Benzyl alcohol	99
26.	Heavy pine oil	—
27.	"Carbitol" acetate	97
28.	Butyl "Carbitol"	96
29.	Butyl "Carbitol" acetate	99
30.	Diglycol diacetate	99
31.	Benzyl "Cellosolve"	99

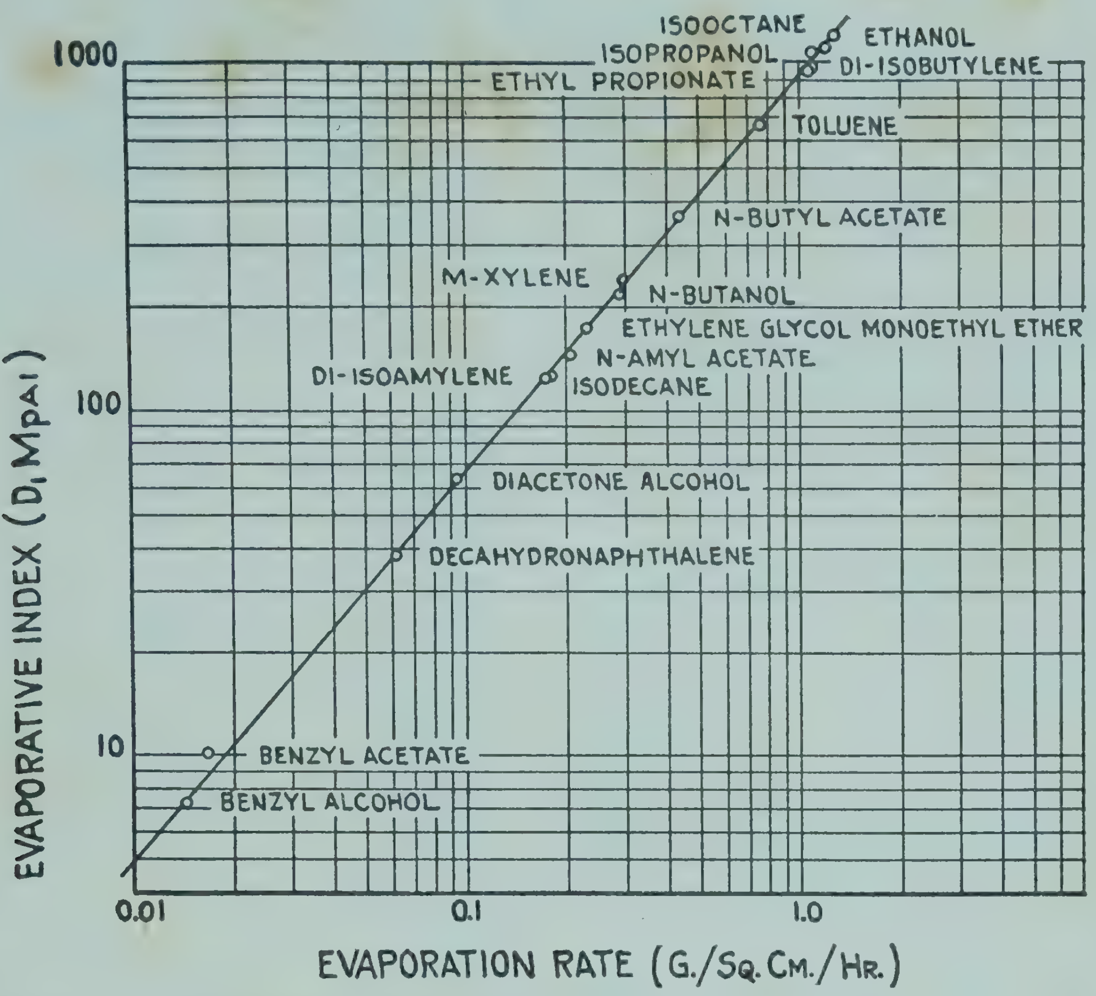


Figure 3.23. Experimental Evaporation Rate Versus Evaporative Index.[12]

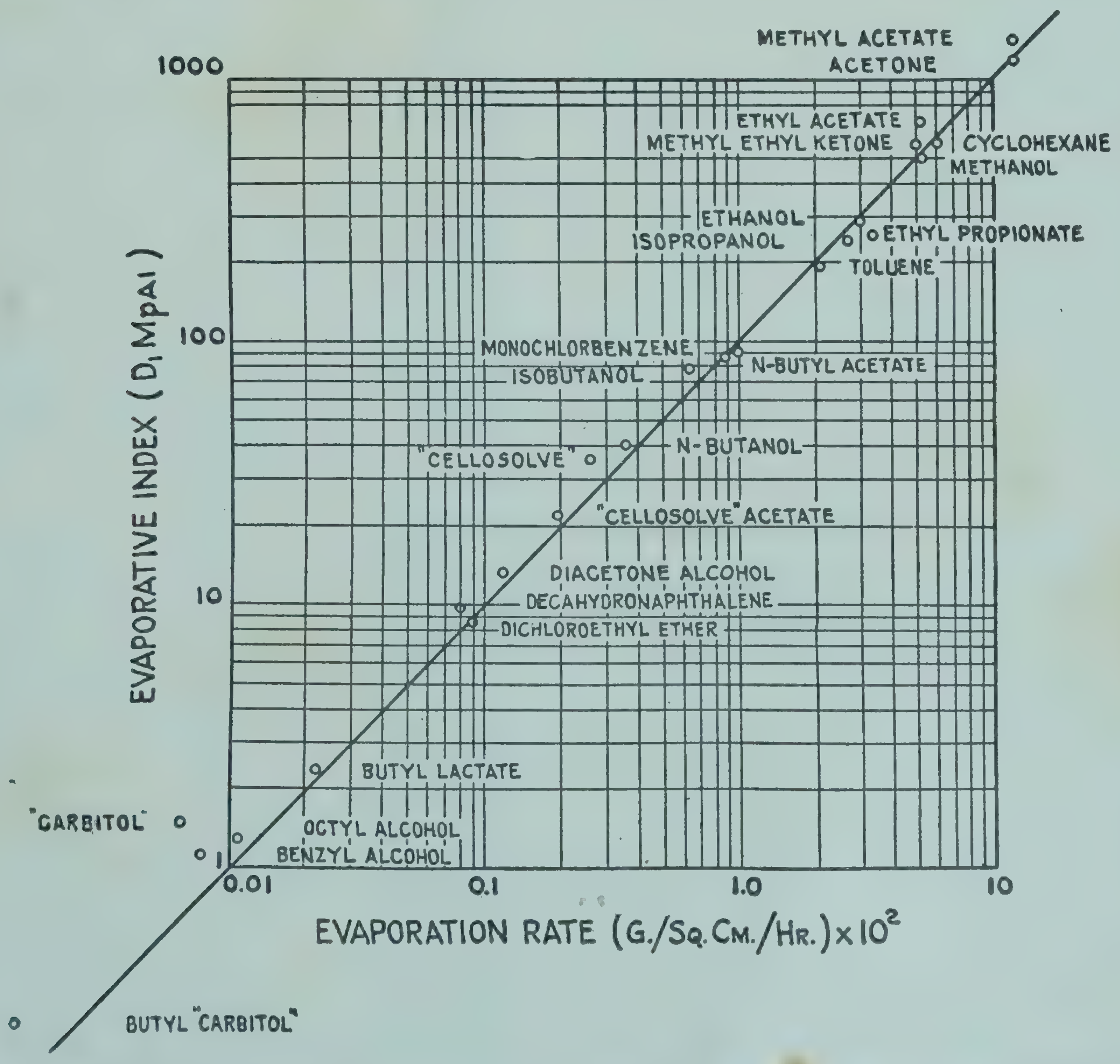


Figure 3.24. Experimental Evaporation Rate Versus Evaporative Index (from data of Doolittle).[12]

TABLE 3.3. EVAPORATION RATES

Solvent	Percentage Evaporated %/hours[a]	Based on *n*-butyl acetate equal to 100.0[a]	Temperature Depression Due to Evaporation (° C.)
Acetone	100/0.72	1365	
Acetonyl acetone	100/200.0		
Amyl acetate			4.35–5
Amyl acetate (mixed isomers)	100/16.0	59	3.9
sec-Amyl acetate		96	
Amyl alcohol (mixed isomers)	100/23.5	35	3.3
sec-Amyl alcohol	100/18.5	47	
Benzene	100/1.26		
Benzyl alcohol	50/500.0		
Benzyl ether of ethylene glycol	hygroscopic		
n-Butyl acetate	100/7.9	100	
sec-Butyl acetate	100/4.35	172–208	8.0
n-Butyl alcohol	100/18.0	38.5	4.8
sec-Butyl alcohol	100/6.6	128	
Butyl butyrate	100/42.0	37.5	
Butyl ether of diethylene glycol	12/500.0 (hygroscopic)		
Butyl ether of diethylene Glycol acetate	5/500.0		
Butyl ether of ethylene glycol	100/130.0	8.0	
Butyl ether of ethylene glycol acetate	100/285.0		
Butyl lactate	100/310.0		
n-Butyl propionate	100/16.0	61.0	4.0
Cyclohexane	100/1.13		
Cyclohexanol	100/225.0		
Cyclohexanone	93/47.0		
Cyclohexanyl acetate	73/60.0		
Decahydronaphthalene	76/60.0		
Diacetone alcohol	100/56.0		
Dichlorethyl ether	84/60.0		
Diethyl carbonate	100/6.4	110	
Diethyl ether of diethylene glycol	94/500.0		
Diethyl ether of ethylene glycol	100/6.3	100	
Diethyl ketone	100/2.7		
Diglycol diacetate	2/500.0		
Diisobutyl ketone	100/44.0		
Dipentene	91/60.0		
Dipropyl ketone	100/17.0		
Ethyl acetate	100/1.4	590	15.6
Ethyl acetoacetate		485	
Ethyl alcohol	100/2.2	308	
Ethyl butyrate	100/4.9		
Ethyl ether of diethylene glycol	51/500.0	51.5	
Ethyl ether of diethylene glycol acetate	34/500.0		
Ethyl ether of ethylene glycol	100/25.0	40	2.8
Ethyl ether of ethylene glycol acetate	100/38.5	25.0	1.9
Ethyl lactate	96/36.5	22.1	
Ethyl propionate	100/2.1	425	
Ethylene dichloride	100/1.4	104.5	
Fenchone	100/103.0		
Furfural	100/49.0		
Furfuryl acetate	99.5/500.0		
Furfuryl alcohol	92/500.0		
Glycol diacetate	100/375		
Hercosol	93/250.0		
Hi-Flash naphtha	100/43.0		
Hexyl acetate	100/16.0	41	
Hexyl (2-ethyl butyl) acetate	100/32.5		
Isobutyl acetate	100/4.6		
Isopropyl acetate	100/1.6	159	

[a] At atmospheric pressure.

TABLE 3.3. EVAPORATION RATES—*Continued*

Solvent	Percentage Evaporated %/hours[a]	Based on *n*-butyl acetate equal to 100.0[a]	Temperature Depression Due to Evaporation (° C.)
Isopropyl alcohol	100/2.6	159	
Isopropyl ether of ethylene glycol	100/32.0		
Isopropyl lactate	97/60.0		
Mesityl oxide		110	
Methanol (anhydrous)	100/1.4		
3-Methoxy butyl acetate	100/58.5		
Methyl acetate	100/0.68	1125	
Methyl acetone	100/0.78		
Methyl amyl acetate	100/17.5		
Methyl amyl alcohol	100/24.0		
Methyl *n*-amyl ketone	100/20.0		
Methyl ethyl ketone		452	
Methylcyclohexone	100/51.0		
Methyl ether of diethylene glycol	55/500.0		
Methyl ether of diethylene glycol acetate	53/500.0		
Methyl ether of ethylene glycol	100/165	56.7	
Methyl ether of ethylene glycol acetate	100/26.0	34.1	
Methyl ethyl ketone	100/1.45		
Methyl *n*-hexyl ketone	88/60.0		
Methyl isobutyl ketone (hexone)	100/4.4		
Methyl propyl ketone	100/2.45	202	
Mineral spirits	100/58.0		
Monochlorobenzene	100/6.9		
Octyl (2-ethyl hexyl) acetate	100/275.0		
Octyl (2-ethyl hexyl alcohol)	80/500		
o-Dichlorobenzene	100/52.5		
Petroleum naphtha	100/2.8		
Phorone	100/125.0		
Pine oil	52/500		
Pine oil (heavy)	45/500.0		
Safe-T-Esso	100/235.0		
Solvesso No. 1	100/3.5		
Solvesso No. 2	100/28.0		
Solvesso No. 3	99.5/500.0		
Tetrahydrofurfuryl alcohol	99/500.0		
Tetrahydronaphthalene	96/500.0		
Toluene	100/3.5	266	10.6
Turpentine (gum spirits)	94/185		
Turpentine (steam-distilled)	95/170		47.5
V.M. & P. naphtha	100/49.0		
Xylene	100/13.5		79.0

	Per cent	
Toluene Butyl acetate Ethyl acetate	65 20 15	10.6
Toluene Butyl propionate Ethyl acetate	65 20 15	10.3
Toluene Butyl acetate	65 35	9.6
Toluene Butyl acetate Amyl acetate (mixed isomers)	65 20 15	9.0
Toluene Butyl acetate Butyl propionate	65 20 15	9.2
Toluene Amyl acetate (mixed isomers)	65 35	8.6

TABLE 3.4. VAPOR PRESSURE (MM HG)

Solvent	20° C.	25° C.	30° C.	35° C.	40° C.	45° C.	50° C.
Benzyl acetate	<0.1	<0.1	<0.1	<0.1	0.1	0.4	0.8
Benzyl alcohol	0.1	0.15	0.2	0.25	0.3	0.7	0.9
Butyl carbitol	<0.1	<0.1	<0.1	<0.1	<0.1	0.1	0.2
sec-Butyl chloroacetate	1.4	1.7	2.0	2.5	3.0	4.5	6.0
n-Butyl formate	22.6	29.4	37.8	48.3	61.3	78.0	98.0
sec-Butyl formate	36.0	48.1	62.5	79.6	102.0	126.0	155.2
"Carbitol"	0.14	0.21	0.29	0.36	0.74	1.02	1.3
Decalin	0.7	1.2	1.5	1.9	2.7	3.7	4.7
Dibutyl phthalate	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Ethyl chloroacetate	3.7	4.9	6.7	8.9	11.7	15.2	19.5
Ethyl formate	206.5	255.0	312.0	382.0	462.0	558.0	668.0
Isobutyl formate	33.0	43.5	56.0	71.0	88.6	111.0	136.0
Isobutyl chloroacetate	3.0	4.3	5.6	7.5	10.0	12.5	16.5
Isopropyl formate	112.0	138.5	174.2	216.0	267.0	325.1	396.0
Methyl formate	500.2	624.5	720.2				
Methyl chloroacetate	6.7	9.0	11.5	15.2	20.0	26.3	33.5
n-Propyl formate	64.5	85.0	107.0	134.0	166.2	203.5	248.0
Terpenyl acetate	<0.1	<0.1	<0.1	0.1	0.14	0.17	0.2

yond the usual values for the individual double bonds to account for the conjugation. No difference is observed whether the double bonds are in the side chains or not provided only that they are congugated. The boiling point of 2-methylene-6-methyl-free-heptane is calculated as follows:

7 carbon atoms in the main chain	5.6
11 hydrogen atoms attached to the main chain	11.0
1 methylene radical	4.4
1 methyl radical	3.05
1 double bond of the type: RCH=CHR	1.9
Conjugation of two double bonds	0.8
B.P.N. calculated	26.75

The B.P.N. of 26.75 gives a calculated boiling point of 145.3° C. whereas the observed boiling point has been recorded as 141.0°C.

"The B.P.N. for the conjugation of three double bonds has been set at 2.4. However, only a few examples are known and this value may require some revision when more boiling points have been ascertained."

Boiling Points of Acetylenes

"The boiling points of the simple acetylenes may be calculated in much the same way as for the olefins. When two conjugated triple bonds are present in the molecule, consideration must be given to whether the triple bonds are at the end of the chain or not. Thus the 1,3-diynes do not require an additional B.P.N., whereas the 2,4-, 3,5-, etc., diynes require an unusually large B.P.N. of 3.0. For conjugated hydrocarbons containing both double and triple bonds, satisfactory results are obtained by using the B.P.N.'s for the conjugated double bonds, although the effect might be expected to be midway between the two."

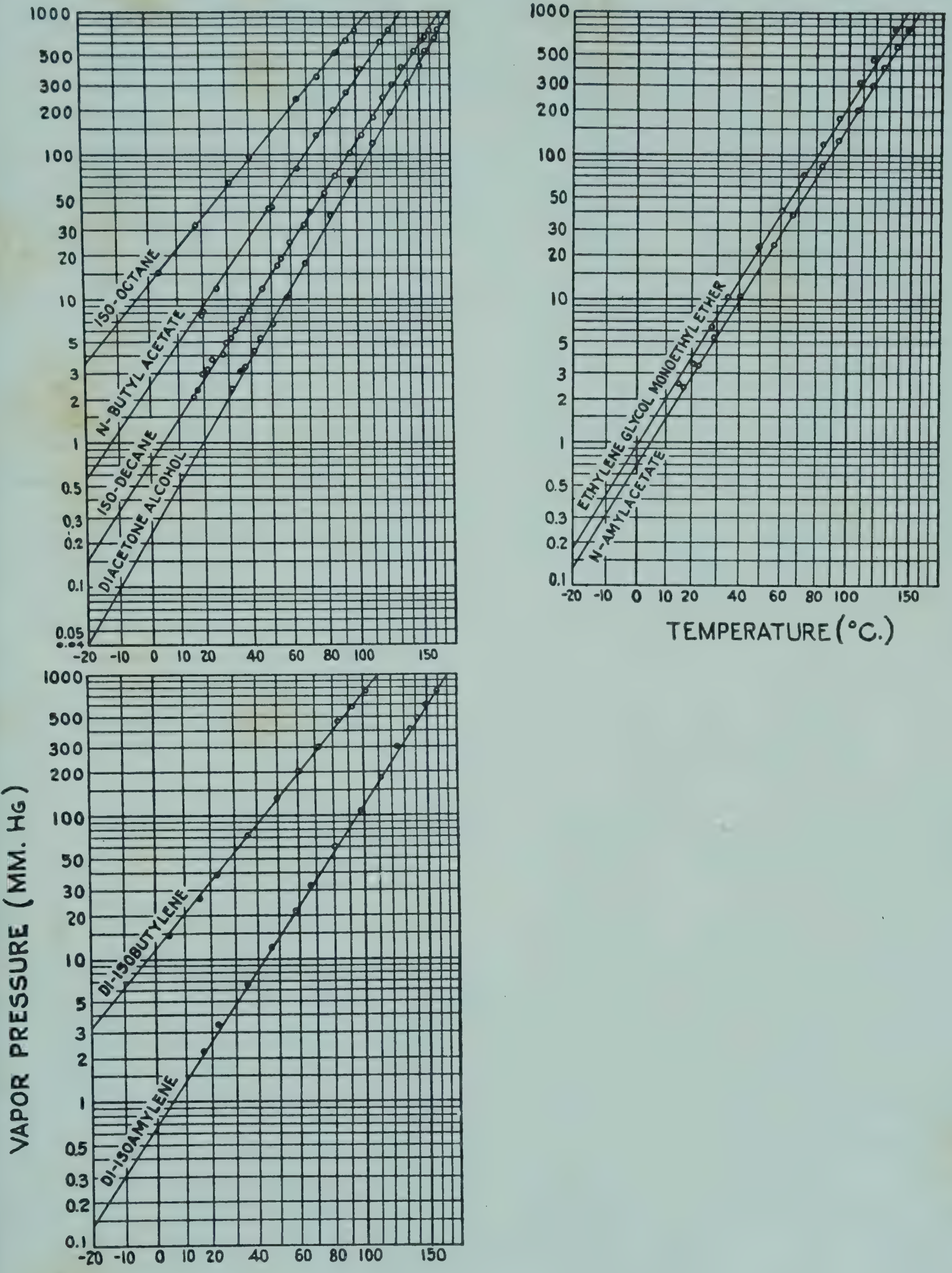


Figure 3.25. Vapor Pressure Curves.[12]

TABLE 3.5. Comparison of Experimental Evaporation Rate and Calculated Evaporative Index[11]

LIQUID	BOILING RANGE (°C)	D_1	M	p_{A1}	D_1Mp_{A1}	E (g/sq cm/hr)
Isooctane	....	0.067	114.1	144	1102	1.197
Isodecane	154.4–159.7	0.060	142.2	15.0	128	0.179
Diisobutylene	100.8–101.9	0.068	112.1	130	994	1.087
Diisoamylene	156.2–161.2	0.061	140.2	14.7	125	0.172
Toluene	109.5–110.5	0.083	94.1	90	685	0.755
n-Xylene	137–139	0.076	106.1	30	241	0.297
Decahydronaphthalene	190–193.5	0.066	138.1	4.2	38.2	0.627
Ethanol (99.8%)	78.3–79.0	0.121	46.1	222	1236	1.245
n-Butanol	116–118	0.090	74.1	33	220	0.288
Isopropanol	98–99	0.102	60.1	177	1091	1.098
Benzyl alcohol	92–94[a]	0.080	108.1	0.85	7.4	0.0143
n-Butyl acetate	123–126	0.073	116.1	44	373	0.437
Ethyl propionate	98–100	0.079	102.1	124	998	1.078
n-Amyl acetate	145–147	0.068	130.1	16.5	146	0.205
Benzyl acetate	100–102[b]	0.067	150.1	1.0	10.1	0.0166
Diacetone alcohol	62–64[c]	0.074	116.1	7.5	64	0.0940
Ethylene glycol monoethyl ether	133–135	0.085	90.1	23	175	0.227

Doolittle's Data

LIQUID	BOILING RANGE (°C)	D_1	M	p_{A1}	D_1Mp_{A1}	$E \times 10^2$ (g/sq cm/hr)
Toluene	109–111	0.074	92.1	28.6	195	2.04
Cyclohexane	80–83	0.074	84.1	96	597	5.93
Decahydronaphthalene	186–194	0.058	138.1	1.2	9.6	0.084
Methanol	64–66	0.130	32.0	125	520	5.03
Ethanol	77–79	0.108	46.1	59	293	2.96
Isopropanol	82–83	0.091	60.1	44	241	2.65
Isobutanol	107–111	0.080	74.1	13.4	79.4	0.64
n-Butanol	116–119	0.080	74.1	6.8	40.3	0.36
Octyl alcohol	182–201	0.058	130.1	0.17	1.28	0.011
Benzyl alcohol	199–204	0.070	108.1	0.15	1.13	0.0066
Methyl acetate	53–55	0.096	74.1	210	1494	11.8
Ethyl acetate	70–80	0.084	88.1	95	703	5.03
Ethyl propionate	90–118	0.070	102.1	36	258	3.31
n-Butyl acetate	119–127	0.065	116.1	11.6	87.5	0.87
Butyl lactate	145–230	0.059	146.1	0.27	2.33	0.022
Acetone	55–57	0.093	58.0	229	1235	11.8
Methyl ethyl ketone	77–82	0.083	72.1	97	580	4.80
Diacetone alcohol	153–160	0.066	116.1	1.7	13	0.12
"Cellosolve"	133–137	0.075	90.1	5.3	35.8	0.26
"Cellosolve" acetate	145–166	0.059	132.1	2.8	21.8	0.195
"Carbitol"	189–203	0.061	134.1	0.18	1.47	0.0066
Butyl "Carbitol"	220–231	0.054	162.1	0.03	0.26	0.0014
Monochlorobenzene	130–134	0.072	112.5	11.5	92.7	0.99
Dichloroethyl ether	172–178	0.064	143.0	0.94	8.6	0.093

[a] At 8 mm. [b] At 10 mm. [c] At 13 mm.

a = proportionality constant
A = subscript referring to component which is diffusing (the vapor of the liquid)
B = subscript referring to stationary component (air) through which diffusion takes place
d = diameter of column (for evaporation in wetted wall columns)
D = diffusion coefficient or diffusivity, sq. cm. + sec.
D_1 = diffusion coefficient under 1 atm. pressure
E = evaporation rate, grams/hour/sq. cm.
h = distance from top of air film to top of container in which evaporation is taking place (for evaporation from flat surfaces)
K = the group $\alpha/RTPx$
k = the group D_1/xuh or AD_1/xud
M = molecular weight
N_A = evaporation rate, gram moles/sec./sq. cm.
P = total pressure, atmospheres
p_{A1} = vapor pressure of evaporating liquid, mm. Hg.
p_{A2} = partial pressure of vapor at air stream side of air film, mm. Hg.
p_{B1} = partial pressure of air at liquid-air film interface, mm. Hg.
p_{B2} = partial pressure of air at air stream side of air film, mm. Hg.
p_{BM} = logarithmic mean of partial pressure of air through film
R = gas constant, 82.07 cc./atm.
T = absolute temperature, ° K.
u = air velocity, cm./sec.
V = volume in gas law, or molecular volume in Gilliland equation
W_A = evaporation rate, grams/sec./sq. cm.
x = distance in direction of diffusion through stagnant film, cm.
y = distance across liquid surface, measured in direction of air flow, cm.

Boiling Points of Naphthenes

"For purposes of calculating the B.P.N.'s and boiling points of the naphthenes, the cyclic part of the molecule is considered to be a radical attached to an open chain hydrocarbon or to hydrogen where there is no aliphatic chain attached to the ring. Fortunately, various groups attached to the ring in addition to the main chain have about the same effect upon the boiling point as when they are attached to the main chain themselves. Consequently, the same B.P.N.'s may be used for groups attached to rings (which are, in turn, attached to the main chain) as when they are attached to the main chain. The effect of the naphthenic ring upon the boiling point is always greater than for the same number of carbon atoms in a normal chain, and additional B.P.N.'s must be used to account for the cyclic structure. These values for the various rings are given in Table 3.6. They fall into two groups, depending upon the ring size. The first contains rings from three to six carbon atoms and the second those with more than six carbon atoms. In the first group the difference between members is only 0.2 unit; in the second group the difference is much larger and amounts to 0.5 for each addi-

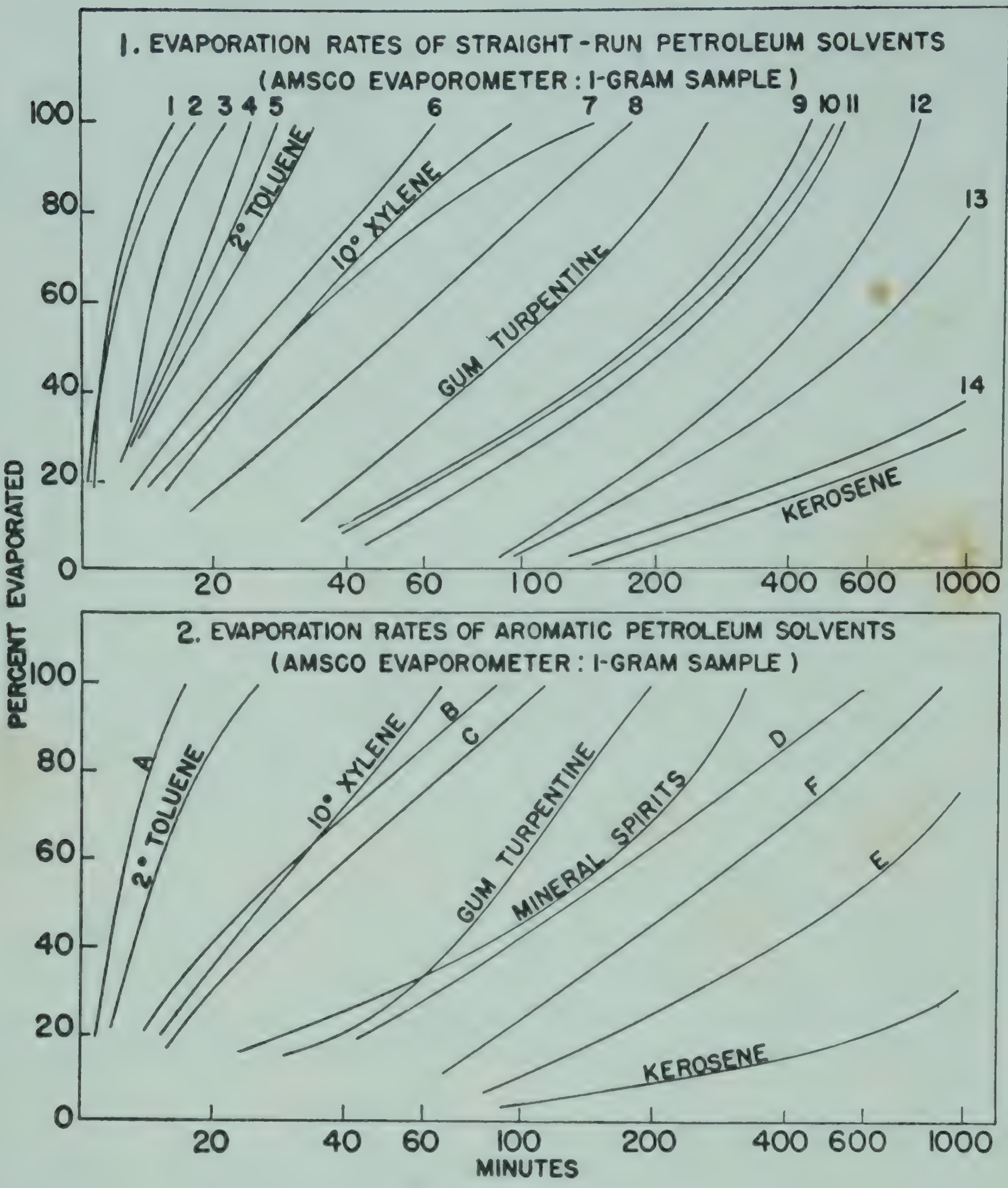


Figure 3:26.[15]

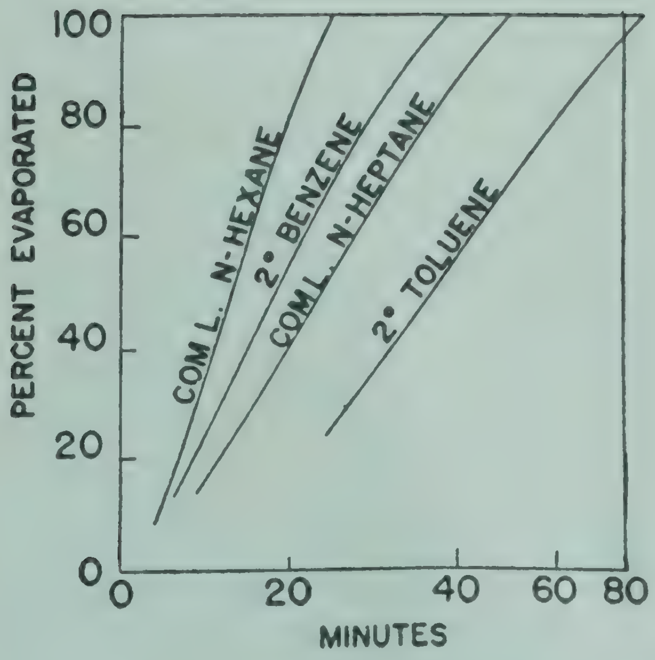


Figure 3.27. Evaporation Rates of Close-Cut Solvents (Amsco Evaporometer; 5-Gram Sample.[15]

TABLE 3.6. Atomic and Group Boiling Point Numbers[14]

STRUCTURAL GROUP	VALUE OF B.P.N.
Carbon, in the main chain	0.8
Hydrogen, attached to the main chain	1.0
Radicals, saturated, attached to the main chain or to cyclic rings	
Methyl	3.05
Ethyl	5.5
Propyl	7.0
Butyl	9.7
2,2-Dimethyl grouping	−0.4
Two or three alkyls attached to adjacent carbons of saturated main chains of 6 carbons or less	+0.5
Four or more alkyls attached to adjacent carbons of saturated main chains of 6 carbons or less	1.0
Type of olefinic linkage	
$CH_2{=}CH_2$	1.2
$RCH{=}CH_2$	1.5
$RCH{=}CHR$	1.9
$R_2C{=}CHR$	2.3
$R_2C{=}CR_2$	2.8
Radicals, unsaturated, attached to main chain	
Methylene	4.4
Ethylidene	7.0
Vinyl	5.4
Propylidene	9.0
Butylidene	10.4
Type of acetylenic linkage	
$HC{\equiv}CH$	4.0
$RC{\equiv}CH$	4.4
$RC{\equiv}CCH_3$	5.4
$RC{\equiv}CR$	4.8
Types of diolefin	
Allenes	4.8
Conjugated, normal values of double bonds plus	0.8
Not conjugated, normal values of double bonds only	
Type of triolefin	
All bonds conjugated, normal values of double bonds plus	2.4
Two bonds conjugated, normal values of double bonds plus	0.8
No conjugation, normal values of double bonds only	
Type of diacetylene	
1,3-Diacetylenes, normal values of triple bonds only	
All other conjugated, normal values of triple bonds plus	3.0
No conjugation, normal values of triple bonds only	
Type of enyne	
Conjugated, normal values of bonds plus	0.8
No conjugation, normal values of bonds only	
Type of dienyne	
Conjugated, normal values of bonds plus	2.4
No conjugation, normal values of bonds only	
Cyclic radicals: Add 0.8 for each carbon, 1.0 for each hydrogen, the normal values of any unsaturated linkages, and the following values for the ring:	
Type 1	
Cyclopropyl	2.1
Cyclobutyl	2.3
Cyclopentyl	2.5
Cyclohexyl	2.7
Type 2	
Cycloheptyl	3.4
Cyclooctyl	3.9
Cyclononyl	4.4
Cyclodecyl	4.9
Cyclohendecyl	5.4
Cyclododecyl	5.9
Cyclotridecyl	6.4
Cyclotetradecyl	6.9
Cyclopentadecyl	7.4
Cyclohexadecyl	7.9
Cycloheptadecyl	8.4

TABLE 3.7 Boiling Point Numbers for the Paraffin Hydrocarbons[13]

Substance	B.P., °C	B.P.N. (obsd.)	B.P.N. (calcd.)		Deviation
A. Normal Hydrocarbons					
0 Hydrogen	−252.8	2.005	0.0 + 2	= 2.0	+0.005
1 Methane	−161.5	4.555	.8 + 4	4.8	−.245
2 Ethane	−88.3	7.71	1.6 + 6	7.6	+.11
3 Propane	−44.5	10.16	2.4 + 8	10.4	−.24
4 Butane	−0.45	13.10	3.2 + 10	13.2	−.10
5 Pentane	+36.2	15.94	4.0 + 12	16.0	−.06
6 Hexane	69	18.80	4.8 + 14	18.8	±.0
7 Heptane	98.52	21.66	5.6 + 16	21.6	+.06
8 Octane	125.8	24.54	6.4 + 18	24.4	+.14
9 Nonane	150.72	27.38	7.2 + 20	27.2	+.18
10 Decane	174	30.24	8.0 + 22	30.0	+.24
11 Hendecane	195.84	33.08	8.8 + 24	32.8	+.28
12 Dodecane	214.5	35.66	9.6 + 26	35.6	+.06
13 Tridecane	234	38.48	10.4 + 28	38.4	+.08
14 Tetradecane	246	40.29	11.2 + 30	41.2	−.91
15 Pentadecane	270	44.16	12.0 + 32	44.0	+.16
16 Hexadecane	287	47.00	12.8 + 34	46.8	+.20
17 Heptadecane	303	49.67	13.6 + 36	49.6	+.07
18 Octadecane	317	52.18	14.4 + 38	52.4	−.22
19 Nonadecane	330	54.58	15.2 + 40	55.2	−.62
B. Methyl Derivatives					
1 2-Methylpropane	−10.2	12.40	2.4 + 7 + 3.05	= 12.45	−0.05
2 2,2-Dimethylpropane	+9.5	13.84	2.4 + 6 + 6.1	14.50	−.66
3 2-Methylbutane	28	15.27	3.2 + 9 + 3.05	15.25	+.02
4 2,2-Dimethylbutane	49	17.02	3.2 + 8 + 6.1	17.30	−.28
5 2,3-Dimethylbutane	58.1	17.82	3.2 + 8 + 6.1	17.30	+.52
6 2,2,3-Trimethylbutane	80.9	19.92	3.2 + 7 + 9.15	19.35	+.57
7 2,2,3,3-Trimethylbutane	106.8	22.50	3.2 + 6 + 12.2	21.40	+1.10
8 2-Methylpentane	60	17.99	4.0 + 11 + 3.05	18.05	−0.06
9 3-Methylpentane	64	18.35	4.0 + 11 + 3.05	18.05	+.30
10 2,2-Dimethylpentane	80.5	19.89	4.0 + 10 + 6.1	20.10	−0.21
11 2,3-Dimethylpentane	89.7	20.77	4.0 + 10 + 6.1	20.10	+.67
12 2,4-Dimethylpentane	83.9	20.21	4.0 + 10 + 6.1	20.10	+.11
13 3,3-Dimethylpentane	86	20.42	4.0 + 10 + 6.1	20.10	+.32
14 2,2,3-Trimethylpentane	110.6	22.91	4.0 + 9 + 9.15	22.15	+.76

TABLE 3.7. *Continued*

SUBSTANCE	B.P., °C	B.P.N. (OBSD.)	B.P.N (CALCD.)		DEVIATION
15 2,2,4-Trimethylpentane	98.5	21.66	4.0 + 9 + 9.15	22.15	−.49
16 2,3,3,4-Tetramethylpentane	130	25.01	4.0 + 8 + 12.2	24.20	+.81
17 2-Methylhexane	90	20.81	4.8 + 13 + 3.05	20.85	−.04
18 3-Methylhexane	91.8	20.98	4.8 + 13 + 3.05	20.85	+.13
19 2,2-Dimethylhexane	106.5	22.48	4.8 + 12 + 6.1	22.90	−.42
20 2,3-Dimethylhexane	113.9	23.24	4.8 + 12 + 6.1	22.90	+.34
21 2,4-Dimethylhexane	110	22.84	4.8 + 12 + 6.1	22.90	−.06
22 2,5-Dimethylhexane	109.2	22.76	4.8 + 12 + 6.1	22.90	−.14
23 3,3-Dimethylhexane	111.5	23.00	4.8 + 12 + 6.1	22.90	+.10
24 3,4-Dimethylhexane	116.5	23.54	4.8 + 12 + 6.1	22.90	+.64
25 2,3,5-Trimethylhexane	129	24.90	4.8 + 11 + 9.15	24.95	−.05
26 2,2,3,4-Tetramethylhexane	156.6	28.10	4.8 + 10 + 12.2	27.0	+1.10
27 2-Methylheptane	116	23.48	5.6 + 15 + 3.05	23.65	−0.17
28 3-Methylheptane	118.8	23.77	5.6 + 15 + 3.05	23.65	+.12
29 4-Methylheptane	118	23.69	5.6 + 15 + 3.05	23.65	+.04
30 2,4-Dimethylheptane	130	25.01	5.6 + 14 + 6.1	25.70	−.69
31 2,5-Dimethylheptane	135	25.57	5.6 + 14 + 6.1	25.70	−.13
32 2,6-Dimethylheptane	134.5	25.52	5.6 + 14 + 6.1	25.70	−.18
33 3,3-Dimethylheptane	137.5	25.86	5.6 + 14 + 6.1	25.70	+.16
34 2,4,6-Trimethylheptane	143	26.49	5.6 + 13 + 9.15	27.75	−1.26
35 3,3,5-Trimethylheptane	159.2	28.40	5.6 + 13 + 9.15	27.75	+0.65
36 3-Methyloctane	142.5	26.43	6.4 + 17 + 3.05	26.45	−.02
37 4-Methyloctane	141.5	26.31	6.4 + 17 + 3.05	26.45	−.14
38 2,4-Dimethyloctane	152.5	27.60	6.4 + 16 + 6.1	28.50	−.90
39 2,5-Dimethyloctane	156	28.03	6.4 + 16 + 6.1	28.50	−.47
40 2,6-Dimethyloctane	158.5	28.32	6.4 + 16 + 6.1	28.50	−.18
41 2,7-Dimethyloctane	160	28.50	6.4 + 16 + 6.1	28.50	±.0

TABLE 3.7. *Continued*

	SUBSTANCE	B.P., °C	B.P.N. (OBSD.)	B.P.N. (CALCD.)		DEVIATION
42	3,6-Dimethyloctane	159.5	28.44	6.4 + 16 + 6.1	28.50	−.06
43	2,4,7-Trimethyloctane	167.5	29.43	6.4 + 15 + 9.15	30.55	−1.08
44	2,6,7-Trimethyloctane	158.5	28.32	6.4 + 15 + 9.15	30.55	−2.23
45	2,2,7,7-Tetramethyloctane	188	32.05	6.4 + 14 + 12.2	32.60	−0.55
46	5-Methylnonane	165	29.12	7.2 + 19 + 3.05	29.25	−.13
47	2,6-Dimethylnonane	174.5	30.31	7.2 + 18 + 6.1	31.30	−.99
48	2,6-Dimethyldecane	194.5	32.91	8.0 + 20 + 3.05	34.10	−1.19
49	2,6,9-Trimethyldecane	207	34.61	8.0 + 19 + 9.15	36.15	−1.54

C. Ethyl Derivatives

1	2-Ethylpentane	93.3	21.13	4.0 + 11 + 5.5 =	20.50	+0.63
2	2-Methyl-3-ethylpentane	114	23.27	4.0 + 10 + 3.05 + 5.5	22.55	+.72
3	3-Methyl-3-ethylpentane	118.8	23.78	4.0 + 10 + 3.05 + 5.5	22.55	+1.23
4	3,3-Diethylpentane	139.2	26.04	4.0 + 10 + 11.0	24.80	+1.24
5	3-Ethylhexane	118.9	23.79	4.8 + 13 + 5.5	23.30	+0.49
6	4-Ethylheptane	139	26.02	5.6 + 15 + 5.5	26.10	−.08
7	6-Methyl-7-ethyldodecane (729 mm.)	241	39.54	9.6 + 24 + 3.05 + 5.5	42.15	−2.61

D. Propyl Derivatives

1	2-Methyl-5-propyloctane	189	32.18	6.4 + 16 + 3.05 + 7.0 =	32.45	−0.27
2	5-Propylnonane	196	33.11	7.2 + 19 + 7.0	33.20	−.09
3	4-Methyl-6-propylhendecane (729 mm.)	235.5	38.71	8.8 + 22 + 3.05 + 7.0	40.85	−2.14
4	6-Propyldodecane (729 mm.)	242	39.68	9.6 + 25 + 7.0	41.60	−1.92

E. Butyl Derivatives

1	5-Butylnonane	218	36.15	7.2 + 19 + 9.7 =	35.90	+0.25

TABLE 3.8. Aliphatic Boiling Point Numbers[13]

DERIVATIVE	B.P.N.	DERIVATIVE	B.P.N.
A. Alkyl Radical	R—	B. Chlorides	Cl—
1 Methyl	3.05	1 RCH_2Cl	7.5
2 Ethyl	5.5	2 R_2CHCl	6.5
3 Propyl	7.0	3 R_3CCl	6.0
4 Butyl	9.7		
C. Alcohols	—OH	D. Ethers	—O—
1 CH_3OH	12.8	1 CH_3OCH_3	3.8
2 RCH_2OH	10.8	2 RCH_2OCH_3, R_2CHOCH_3, R_3COCH_3	2.9
3 R_2CHOH	8.8	3 RCH_2OCH_2R, R_2CHOCH_2R, R_3COCH_2R	2.0
4 R_3COH	6.8	4 $R_2CHOCHR_2$, R_3COCHR	1.1
		5 R_3COCR_3	(0.2?)
E. Aldehydes	=O	F. Ketones	=O
1 $HCHO$, CH_3CHO	8.8	1 CH_3COCH_3	8.5
2 RCH_2CHO	8.2	2 RCH_2COCH_3	8.0
3 R_2CHCHO	7.6	3 $R_2CHCOCH_3$, RCH_2COCH_2R	7.5
4 R_3CCHO	7.0	4 R_3CCOCH_3, $R_2CHCOCH_2R$	7.0
		5 R_3CCOCH_2R, $R_2CHCOCHR_2$	6.5
		6 R_3CCOCH_2R	(6.0?)
		7 R_3CCOCR_3	(5.5?)
G. Acids	—COOH	H. Esters	—OO—
1 $HCOOH$, CH_3COOH	20.0	1 $HCOOCH_3$, CH_3COOCH_3	9.4
2 RCH_2COOH	19.3	2 RCH_2COOCH_3, CH_3COOCH_2R	8.5
3 $R_2CHCOOH$	18.6	3 $R_2CHCOOCH_3$, RCH_2COOCH_2R, $HCOOCHR_2$, $CH_3COOCHR_2$	7.6
4 R_3CCOOH	17.9	4 $R_3CCOOCH_3$, $R_2CHCOOCH_2R$, $RCH_2COOCHR_2$, $HCOOCR_3$, CH_3COOCR_3	6.7
		5 $R_3CCOOCH_2R$, $R_2CHCOOCHR_2$, RCH_2COOCR_3	5.8
		6 $R_3CCOOCHR_2$, $R_2CHCOOCR_3$	4.9
		7 $R_3CCOOCR_3$	4.0

TABLE 3.8. *Continued*

DERIVATIVE	B.P.N.	DERIVATIVE	B.P.N.
I. Primary Amines	$-NH_2$	J. Secondary Amines	$-NH-$
1 CH_3NH_2	8.4	1 CH_3NHCH_3	6.0
2 RCH_2NH_2	7.3	2 RCH_2NHCH_3	5.0
3 R_2CHNH_2	6.2	3 $R_2CHNHCH_3$, RCH_2NHCH_2R	4.0
4 R_3CNH_2	5.1	4 R_3CNHCH_3, $R_2CHNHCH_2R$	3.5
		5 R_3CNHCH_2R, $R_2CHNHCHR_2$	3.0
K. Tertiary Amines	$=N-$		
1 $CH_3N(CH_3)_2$	2.5		
2 $RCH_2N(CH_3)_2$	2.0		
3 $R_2CHN(CH_3)_2$, $(RCH_2)_2NCH_3$	1.5		
4 $R_3CN(CH_3)_2$, $(R_2CH)_2NCH_3$, $(RCH_2)_3N$	1.25		
L. Cyanides	$-CN$	M. Isocyanide	$-NC$
1 CH_3CN	15.2	1 CH_3NC	13.3
2 RCH_2CN	14.0	2 RCH_2NC	12.2
3 R_2CHCN	12.8	3 R_2CHNC	11.1
4 R_3CCN	11.6	4 R_3CNC	10.0

TABLE 3.9

SUBSTANCE	B.P.N. (CALCD.)	B.P. (CALCD.)	B.P. (OBSD.)	B.P.N. (OBSD.)
1 1-Chloropentane	$4.0 + 11 + 7.5 = 22.5$	106.7	108.35	22.67
2 2-Chloropentane	$4.0 + 11 + 6.5 = 21.5$	96.9	96.7	21.48
3 3-Chloropentane	$4.0 + 11 + 6.5 = 21.5$	96.9	97.3	21.54
4 1-Chloro-2-methylbutane	$3.2 + 8 + 3.05 + 7.5 = 21.75$	99.4	98.3	21.64
5 2-Chloro-2-methylbutane	$3.2 + 8 + 3.05 + 6.0 = 20.25$	84.3	86.0	20.41
6 3-Chloro-2-methylbutane	$3.2 + 8 + 3.05 + 6.5 = 20.75$	89.4	91.0	20.91
7 4-Chloro-2-methylbutane	$3.2 + 8 + 3.05 + 7.5 = 21.75$	99.4	99.6	21.77
8 1-Chloro-2,2-dimethylpropane	$2.4 + 5 + 6.10 + 7.5 = 21.0$	92.0	84.4	20.26

TABLE 3.10. Boiling Point Deviations[14]

Type of Hydrocarbon	No. of Hydrocarbons Considered	Av. Deviation from Calcd., Irrespective of Sign, °C.	Deviation of Av., Considering Sign, °C	% of B.P.'s within ± 10°C of Calcd.
Paraffin	108	3.26	−0.15	91.4
Olefin	160	3.51	−0.79	92.5
Diolefin	117	3.98	−0.69	94.8
Triolefin	13	11.25	+2.16	69.2
Acetylene	32	3.71	−0.71	87.5
Diyne	12	3.74	+0.62	100.0
Enyne and dienyne	15	10.54	−7.02	60.0
Naphthene (all types)	305	4.08	−0.02	93.7
Total	762	4.06	−0.42	91.8

tional carbon atom introduced into the ring. This may indicate that the larger rings in the second group have a different type of structure. It is also interesting to note that the disubstituted double bond, RCH═CHR, has a B.P.N. 0.2 unit lower than the cyclopropyl group, which makes a smooth series with the cyclic compounds.

"The B.P.N.'s of the cyclic radicals have been determined on the basis that the ring be considered to be attached in all cases to the end of the aliphatic chain. If this is not actually the case, the portion of the chain left over is considered to be an alkyl radical and is assigned the usual B.P.N. characteristic of the radical. This is the only way that satisfactroy results can be obtained without resorting to the use of a large number of B.P.N.'s for the different rings attached at various points along the main chain because in nearly all of the hydrocarbons appearing in the literature, the ring is larger than that portion of the chain relegated to a radical. This is desirable because the boiling point of an organic molecule is a function of its length, in part.

"The method of calculating the B.P.N. of a simple naphthene may be demonstrated with 1-methyl-2-isopropylcyclopentane. The cyclopentyl radical is attached to the second carbon of the propane chain, which is the longest open chain in the molecule; consequently, when the B.P.N. is calculated, the hydrocarbon should be considered to be a derivative of ethane to one end of which is attached a cyclopentyl and a methyl radical. The B.P.N. of the cyclopentyl radical is obtained by adding the B.P.N.'s of the five carbon and eight hydrogen atoms and the B.P.N. characteristic of the ring size. The calculation of the B.P.N. follows:

2 carbon atoms in the main chain	1.6
4 hydrogen atoms attached to the main chain	4.0
2 methyl radicals	6.1
1 cyclopentyl radical less one hydrogen atom: 4.0 + 8 + 2.5 = 14.5.	14.5
B.P.N. calculated	26.2

The B.P.N. of 26.2 gives a calculated boiling point of 140.6°; the observed boiling point is 142.5° C."

"The calculation of the boiling points of the unsaturated cyclic hydrocarbons follows the same general procedure; B.P.N.'s are employed for the various types of ethylenic linkages in Table 3.6 regardless of whether they occur in the open or closed portions of the molecule. The boiling point of 5-methyl-1-allyl-1-cyclohexane may be calculated by way of example. There are three carbon atoms in the main chain, the allyl group. The double bond in this portion of the molecule belongs to the $RCH{=}CH_2$ type which take B.P.N. of 1.5. The double bond in the cyclohexenyl radical is of the $R_2C{=}CHR$ type, and the value 2.3 is required. The double bonds are not conjugated and no additional B.P.N. is needed for them. The methyl group attached to the cyclohexenyl radical has its usual value of 3.05. The B.P.N. of the ring is obtained by adding together the values for six carbons, eight hydrogens, and the value of the six-carbon ring:

3 carbon atoms in the main chain	2.4
5 hydrogen atoms attached to the main chain	5.0
1 double bond of the type $RCH{=}CH_2$	1.5
1 double bond of the type $R_2C{=}CHR$	2.3
1 methyl radical	3.05
1 cyclohexenyl radical, less the hydrogens misplaced and the double bond: $4.8 + 8.0 + 2.7 = 15.5$	15.5
B.P.N. calculated	29.75

The B.P.N. of 29.75 gives a calculated boiling point of 170.1° C; the observed boiling point is 172.0° C."

"Boiling points have been calculated for all 762 of the aliphatic hydrocarbons for which boiling points at approximately 760 mm are recorded in the literature, and the values are compared. These results are summarized in Table 3.10. The accuracy of the method of calculating boiling points is indicated by the fact that over 90 per cent of the observed boiling points fall within +10° C of the calculated, whereas the average deviation is only 4.06° C. in spite of individual variations as large as 61.7°. The most unsatisfactory correlations were obtained with the triolefin and the enyne-dienyne groups. Since these classes are small and not well known, it appears probable that many of the boiling points which have been recorded for them are not accurate or that their structures were not determined correctly. For all other groups the data are satisfactory, in general, especially those for the cyclic hydrocarbons which comprise all types of derivatives of both saturated and unsaturated rings, including terpenes and the like."[14]

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Chapter 4

Viscosity

Viscosity is the internal friction which causes the differences in mobility of liquids or their resistance to flow. This property is of considerable interest and importance to many industries. In the making of lacquers it is determined by such influences as the species of cotton used as the source of nitrocellulose, the locality where it is grown, its ripeness, the method used in making the cellulose derivative, the pressing, the concentration, etc. For many years it was impossible to make nitrocellulose of low viscosity, which seriously hindered the widespread use of lacquers. Worden[1] lists the following procedures and substances which reduce the viscosity of cellulose ethers and esters:

1. The addition of solvents or solvent plasticizers such as acetone, chloroform, tricresyl phosphate, diethyl phthalate, dibutyl tartrate and phenyl benzoate.
2. Heating the dissolved esters or ethers with or without pressure.
3. Treating the dry, or moist cellulose derivative or its solution with dilute acid or the acid gas.
4. Disintegrating cellulose or subjecting it to ultraviolet light.
5. Over-ripening.
6. Addition of ethyl alcohol containing 0.1 per cent acetic acid and then treating with ultraviolet light.
7. Addition of water or acid to the solution of cellulose ethers and esters.
8. Addition of gall or bile.

With the newer types of low-viscosity nitrocellulose, it is possible to load lacquers with resins or pigments, which give the film body, strength and resistance to wear. Loading also produces quicker setting because evaporation of the solvent mixture brings about a quick rise in consistency. A shorter setting time is effected by increased loading. This establishes an interrelation between the degree of loading, viscosity and setting time. Viscosities in spraying lacquers must not be high, since they will require high spraying pressures which produce undesirable behavior in the lacquer.

Mardles[3] found that there is a relationship between solvent power and viscosity. The optimum solvent mixture dissolves the cellulose ester most rapidly, yields the least viscous solution, and produces a high degree of dispersion. Nonsolvents, on the other hand, increase viscosities provided their admixture does not result in increased solvency. The more powerful a

TABLE 4.1. EFFECT OF AGING ON CONSISTENCY OF VARIOUS LACQUERS[4]

NO.	DESCRIPTION OF LACQUER	KEPT IN ROOM			KEPT IN INCUBATOR		
		Consistency		Reduction	Consistency		Reduction
		May 16	August 8		May 16	August 8	
		Seconds	*Seconds*	*Per cent*	*Seconds*	*Seconds*	*Per cent*
1	Blank (10% nitrocellulose in solvents)	124[a]	105	15	124	92	26
2	Blank (10% nitrocellulose in solvents)	124	103	17			
3	Blank 0.1% pyridine	106	67	36			
4	Blank in tin can	131	111	16	134	97	28
5	Blank + 0.2% urea	123	110	11	123	92	26
6	Blank + 0.2% urea	122	110	11	122	92	26
7	Blank + 0.2% urea	122	109	11	122	90	26
8	Blank + 0.2% urea	125	117	7	126	99	22
9	Blank + 5% ZnO	150	105	30			
10	Blank + 5% TiO_2 + $BaSO_4$ pigment	119	107	10			
11	Blank + 2.5% chrome yellow pigment	128	111	12			
12	Blank + 1.2% Prussian blue pigment	121	105	13			
13	Black auto lacquer	118	99	15			
14	10 grams cotton + 40 cc. butyl acetate + 40 cc. toluene + 20 cc. butyl alcohol	217	206	4	217	171	21
15	Adherence standard	120	110	8	120	93	23
16	Commercial brushing lacquer 1				79	68	14
17	Commercial brushing lacquer 2				135	103	20
18	Blank + 20% Ester gum	122	80	35			
19	Blank + 20% Dammar	130	110	15			
20	Blank + 5% butyl phenolate	116	101	13			
21	12 grams nitro-cellulose in 100 cc. butyl acetate	159	135	15			
22	12 grams nitro-cellulose in 100 cc. ethyl acetate	80	69	13			

[a] The original value in each test was taken approximately 1 week after the solutions were made.

solvent, the more closely does a solution obtained with it approach a true solution. In the case of an ether-alcohol mixture containing 4 per cent of nitrocellulose of 12.2 per cent nitrogen content, Gibson and McCall[5] found that minimum viscosities are obtained when the alcohol content ranges from 40 to 55 per cent and the ether 60 to 45 per cent by volume. It is thus evident that ethyl alcohol materially reduces the viscosity of a nitrocellulose solution; and butyl alcohol behaves in the same manner. A mixture of alcohol and acetone, or of benzene and acetone, will also reduce viscosities. Maximum results are obtained when the alcohol content is about 14.5 per cent

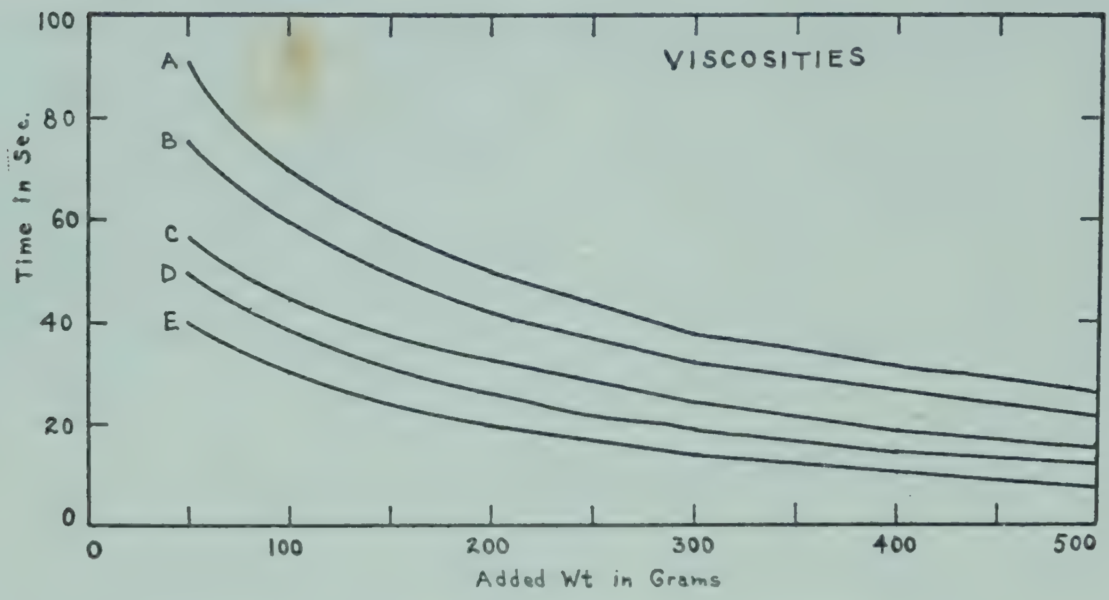

Figure 4.1. Viscosity[6] at Room Temperature:
A, ½-sec. nitrocellulose
B, ½-sec. nitrocellulose + 10% turpentine
C, ½-sec. nitrocellulose + 10% toluene
D, ½-sec. nitrocellulose + 10% xylene
E, ½-sec. nitrocellulose + 10% butyl acetate

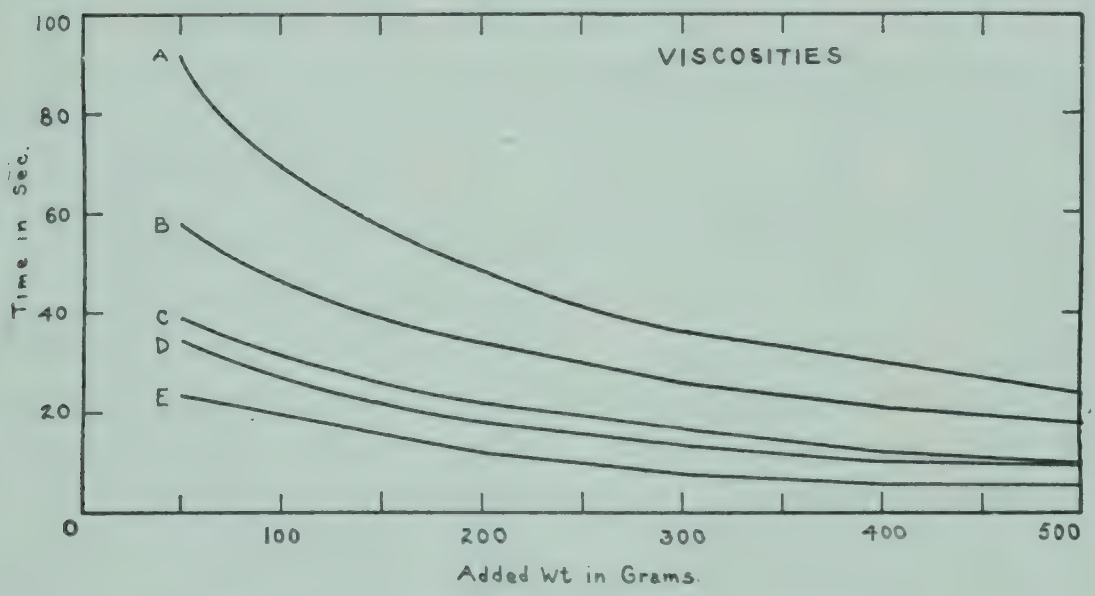

Figure 4.2. Viscosity[6] at Room temperature:
A, ½-sec. nitrocellulose
B, ½-sec. nitrocellulose + 20% turpentine
C, ½-sec. nitrocellulose + 20% toluene
D, ½-sec. nitrocellulose + 20% xylene
E, ½-sec. nitrocellulose + 20% butyl acetate

of the alcohol-acetone mixture and the benzene content about 16.5 per cent of benzene in the benzene-acetone mixture. Esters, owing to their solvent power, yield low-viscosity solutions. Fifteen per cent is usually the minimum limit, and any amount less than this will produce only a slight drop in viscosity. However, any amount above 15 per cent will reduce the viscosity until the limit is reached. Commercial butyl acetate, as compared with the refined ester, is twice as strong in its power to lower the viscosity of nitrocellulose solutions. This is attributed to the presence of butyl alcohol in the

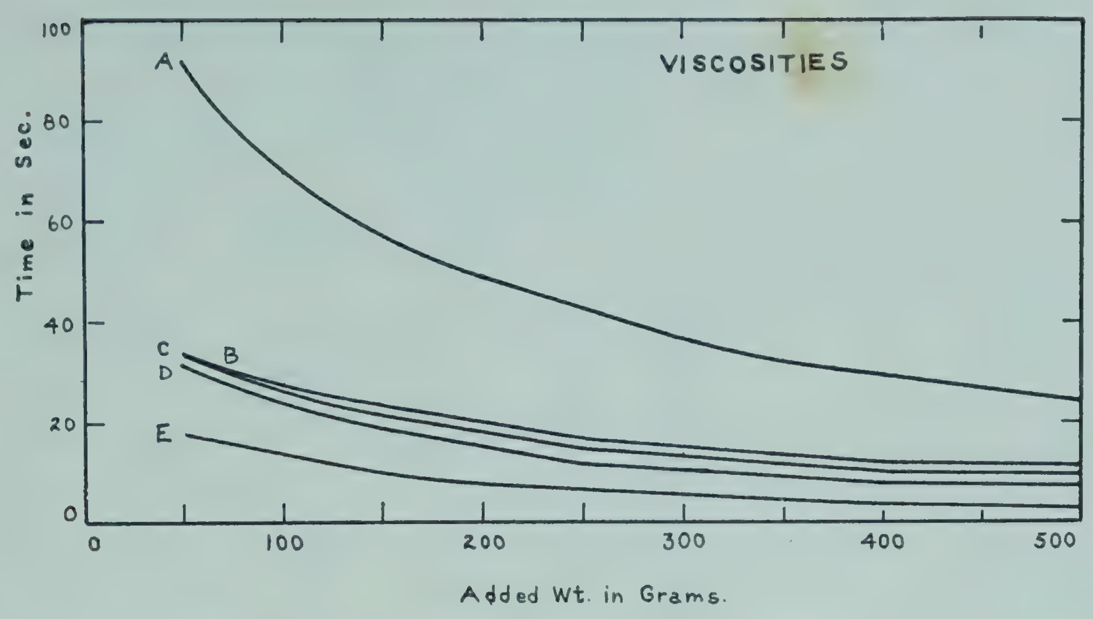

Figure 4.3. Viscosity[6] at Room Temperature:
A, $\frac{1}{2}$-sec. nitrocellulose
B, $\frac{1}{2}$-sec. nitrocellulose + 30% turpentine
C, $\frac{1}{2}$-sec. nitrocellulose + 30% toluene
D, $\frac{1}{2}$-sec. nitrocellulose + 30% xylene
E, $\frac{1}{2}$-sec. nitrocellulose + 30% butyl acetate

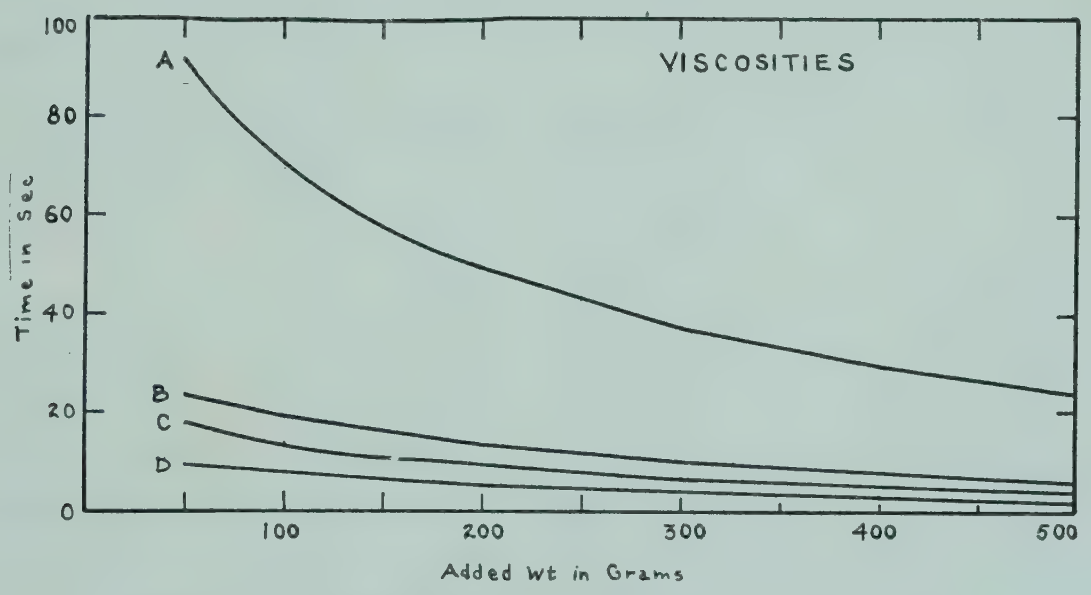

Figure 4.4. Viscosity[6] at Room Temperature:
A, $\frac{1}{2}$-sec. nitrocellulose
B, $\frac{1}{2}$-sec. nitrocellulose + 40% toluene
C, $\frac{1}{2}$-sec. nitrocellulose + 40% xylene
D, $\frac{1}{2}$-sec. nitrocellulose + 40% butyl acetate

commercial grade. Benzene in the presence of pure ester merely acts the part of diluent; but when mixed with alcohol, it becomes a solvent and acquires the power to reduce viscosity. In general, solvents of low boiling point, low vapor pressure, and high solvency yield solutions of low viscosity, and conversely increase in vapor pressure and boiling point and decrease in solvency give an increase in viscosity. These facts are of especial significance in a homologous series.

Marling and Purdy[6] determined the effect of thinners on the consistency of nitrocellulose. The results are reported in Figs. 4.1 through 4.4. The solution consists of 25 per cent nitrocellulose and 75 per cent solvent. The

TABLE 4.2. VISCOSITY DATA

No.	Description of Lacquer		Series I—45 Days[a]			Series II—125 Days[a]		
			Consistency			Consistency		
			April 30	June 16	Reduction	March 10	July 16	Reduction
		cc.	Seconds	Seconds	Per cent	Seconds	Seconds	Per cent
	24 grams 1/2-second nitrocellulose in:							
1	Butyl acetate	200	100	75	25	273	215	21
2	Ethyl acetate	200	49	37	24	138	112	19
3	Diacetone alcohol	200	253	169	33			
4	Ethyl lactate	200	211	170	20			
5	Butyl acetate + toluene	100 100	126	96	25	409	316	21
6	Butyl acetate + toluene	160 140	140	105	25	748	545	27
7	Butyl acetate + benzene	100 100	134	107	20	433	321	26
8	Butyl acetate + ethyl alcohol	100 100	113	97	14	295	239	22
9	Butyl acetate + butyl alcohol	100 100	168	135	20	476	242	49
10	Butyl acetate + Ester gum, 50%	150 48	203	148	27	688	460	33
11	Butyl acetate + Dammar, 50%	150 48	137	83	40	375	283	25
12	Butyl acetate + tricresyl phosphate	200 12	102	82	20			
13	Butyl acetate Butyl phenolate	200 12	126	101	20	336	246	27
14	Butyl acetate kept in incubator at 97° F. (36° C.)	200	114	76	33	415	186	55
	12 grams 12-second nitrocellulose in:							
15	Butyl acetate	300	125	95	24			
16	Ethyl acetate	300	59	46	22			
17	Diacetone alcohol	300	203	157	23			
18	Ethyl lactate	300	246	209	15			
19	Butyl acetate + toluene	150 150	200	124	38			
20	Butyl acetate + lactic acid, 0.5%	300	120	98	18			
21	Butyl acetate + acetic acid, 0.5%	300	127	83	35			
22	Butyl acetate + nitric acid, 0.5%	300	108	90	17			
23	Butyl acetate + ammonium hydroxide, 0.17%	300	116	46	60			
24	Butyl acetate saturated with urea	300	106	78	26	415	375	5
25	Butyl acetate + tricresyl phosphate, 6 grams	300	155	80	48			
26	Butyl acetate + butyl phenolate, 6 grams	300	133	85	36			
27	Butyl acetate kept in sunlight	300	125	77	42			
28	100 cc. 4-second stock solution + 50 cc. ethyl acetate + 50 cc. benzene		166	148	11			
29	70 cc. 1/2-second nitrocellulose stock + 80 cc. ethyl acetate + 50 cc. benzene		523	520				
30	24 grams. A.S. nitrocellulose in 200 cc. ansol		215	157	26			
31	24 grams 1/2-second nitrocellulose in 200 cc. butyl acetate (80% saturated with H_2O)		101	95	6			
32	12 grams 12-second nitrocellulose in 300 cc. butyl acetate + 5 cc. NaOH in butyl alcohol		84	52	38			
33	24 grams 1/2-second nitrocellulose in 100 cc. butyl acetate + 100 cc. toluene + 0.05 gram pyridine					427	210	51

[a] All tests made in the dark, except where otherwise specified.

solvent is 50 per cent ethyl alcohol-butyl acetate and 50 per cent toluene by volume. They found that the consistency of one-half second, four-second, and ten-second nitrocellulose is reduced by increasing the amount of thinner.

Excellent results were obtained in the researches of McArdle and Baldeschwieler[8] in the qualitative test for petroleum solvent naphthas. They express graphically such relationships as viscosity and boiling point, solvency and boiling point, etc.

The viscosity of resin solutions is practically constant in benzene, toluene and xylene. A higher viscosity is obtained in saturated hydrocarbons than in unsaturated. Viscosities of oleo-varnishes are reduced in proportion to the volume ratios of the thinners used. The more powerful a solvent, the greater is the reduction of viscosity.

Bachinskii[9] was first to realize that a definite relationship exists between the volume and the fluidity of liquids. But not having sufficient data at hand, he was unable to give a true mathematical expression of his theory. However, since his time others have taken up this study; Bingham, Adams and McCauslin[10] have made the largest contribution to it, and they arrived at the following conclusions:

"1. The fluidity-volume curves of the aliphatic alcohols follow the hyperbolic equation of the form

$$V = A\varphi - B/(\varphi + D) + C$$

whether the change in volume is due to the variation of temperature or pressure. It also becomes the earlier Bachinskii equation when $\varphi + D$ is large in respect to B.

2. To lower the fluidity a given amount requires a quite different reduction in the volume depending upon whether it is brought about by pressure or by cooling. This curious and very important difference may be explained as the result of the high elasticity of the atoms and molecules. According to this view, at the lowest practicable pressure, *i.e.*, the vapor pressure of the liquid, the constant $[C]_P$ represents the volume of the molecules in one mole in the loosest form of close packing, at which the fluidity must be zero. On compression, with the fluidity remaining at zero, the molar volume is gradually reduced to its minimal value of $[C]_T$.

3. The minimal molar volume for zero fluidity is independent of the temperature of the liquid, of course in the undercooled state. Whereas this minimal volume, V_0, like the absolute zero of temperature, may seem remote or even somewhat hypothetical, nevertheless its value is obtained from reliable data as a constant which can be made precise. From the limited data available, it appears that this minimal volume may be calculated from atomic constants, *e.g.*, 0 = 1.55; C = 2.94; H = 5.65; Br = 18.41; I = 23.82; and S = 20.13.

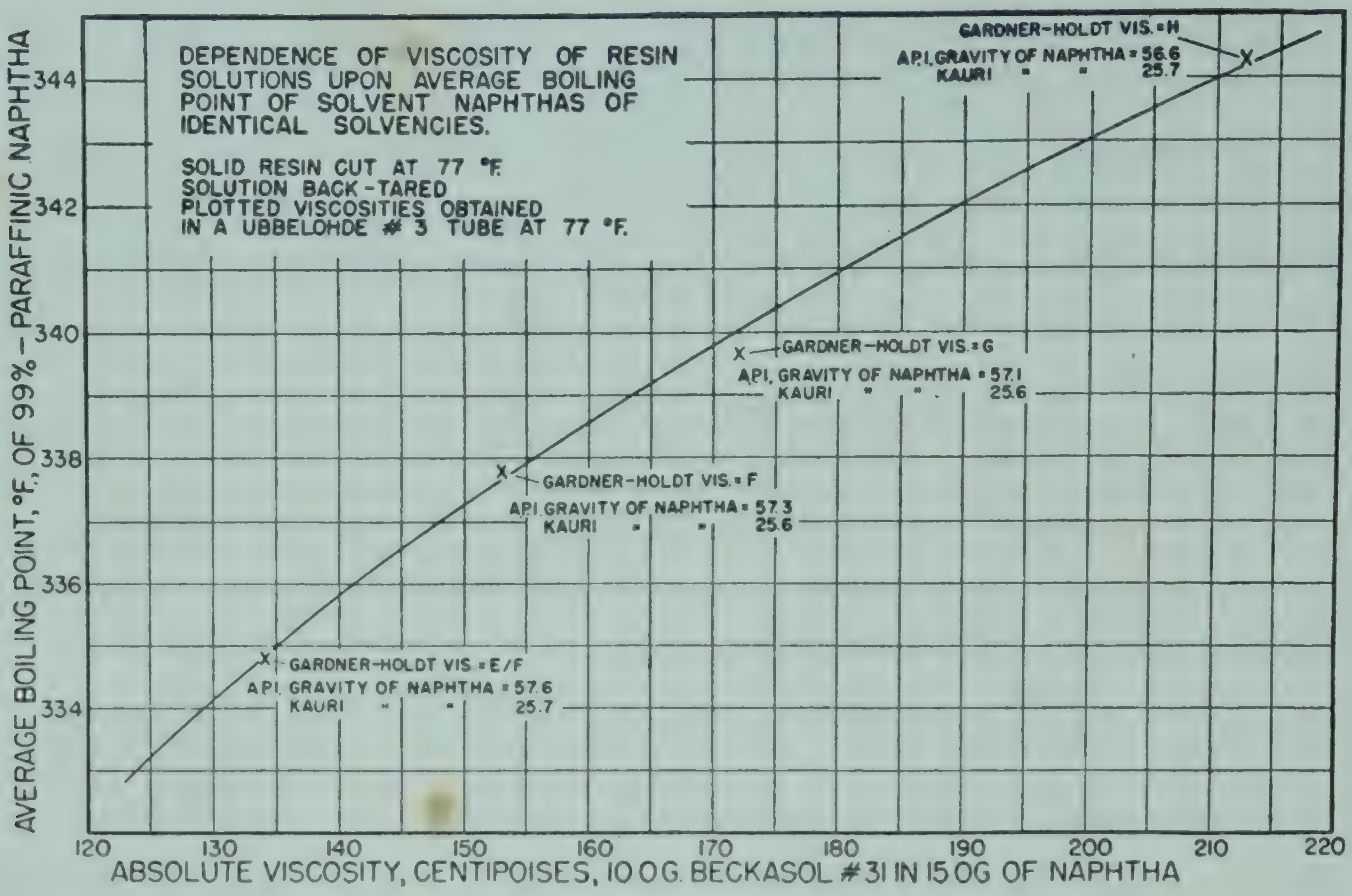

Figure. 4.5.[8]

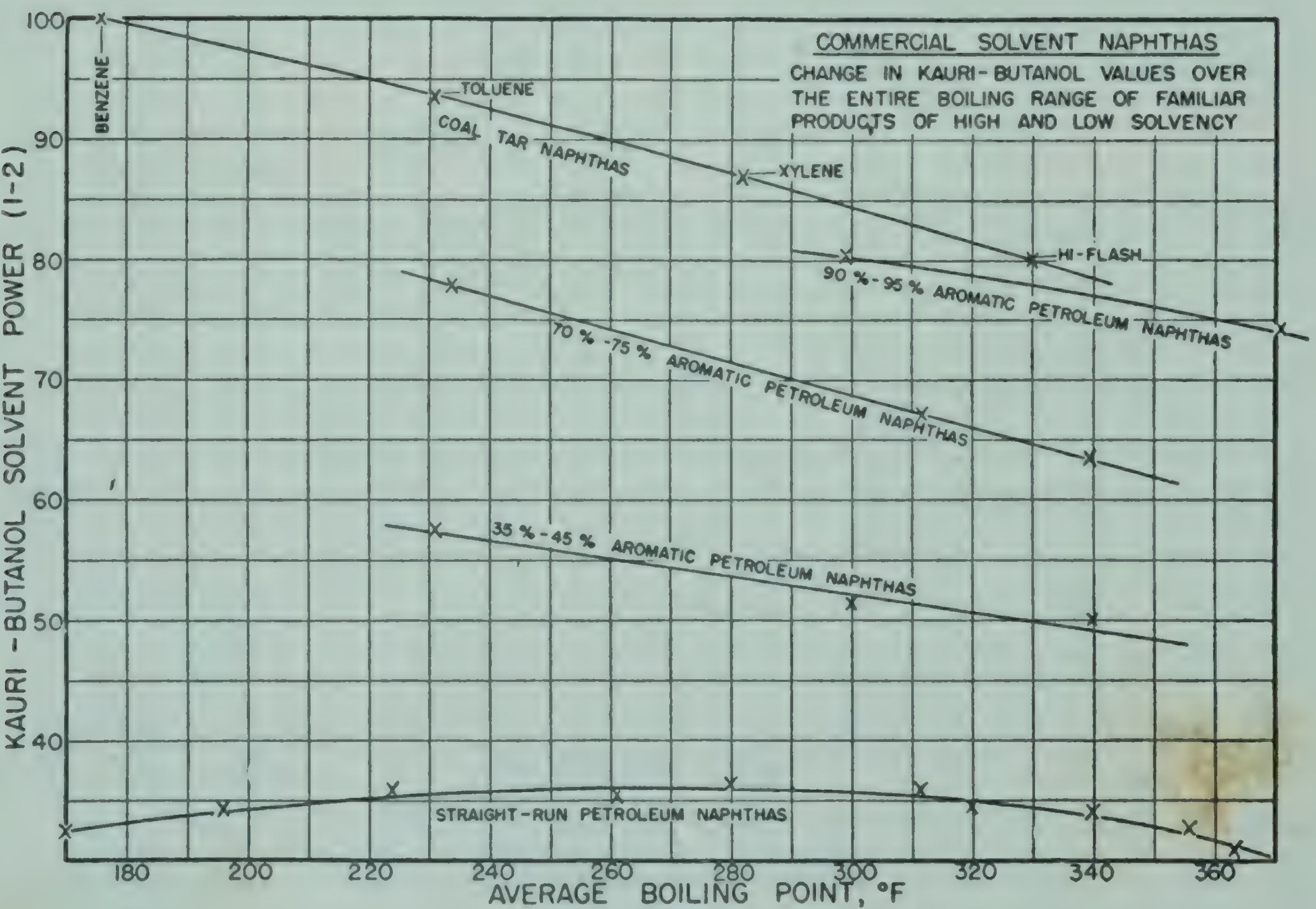

Figure 4.6.[8]

4. When the monatomic liquid, mercury, is heated, the volume varies as a linear function of the temperature centigrade, t. This becomes a direct proportionality when 272.8° is added to the temperature.

5. The fluidity of mercury varies linearly with the molar volume either

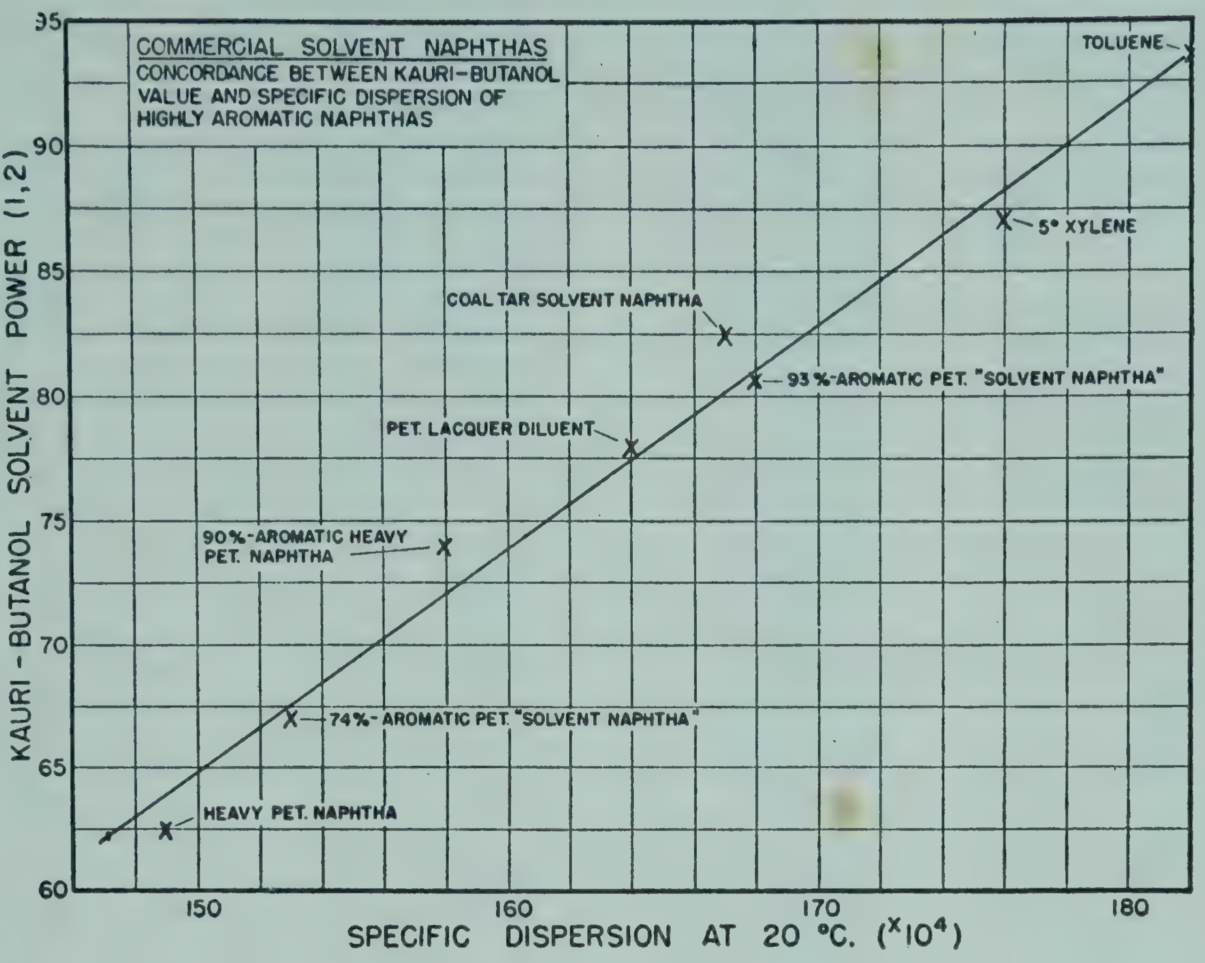

Figure 4.7.[8]

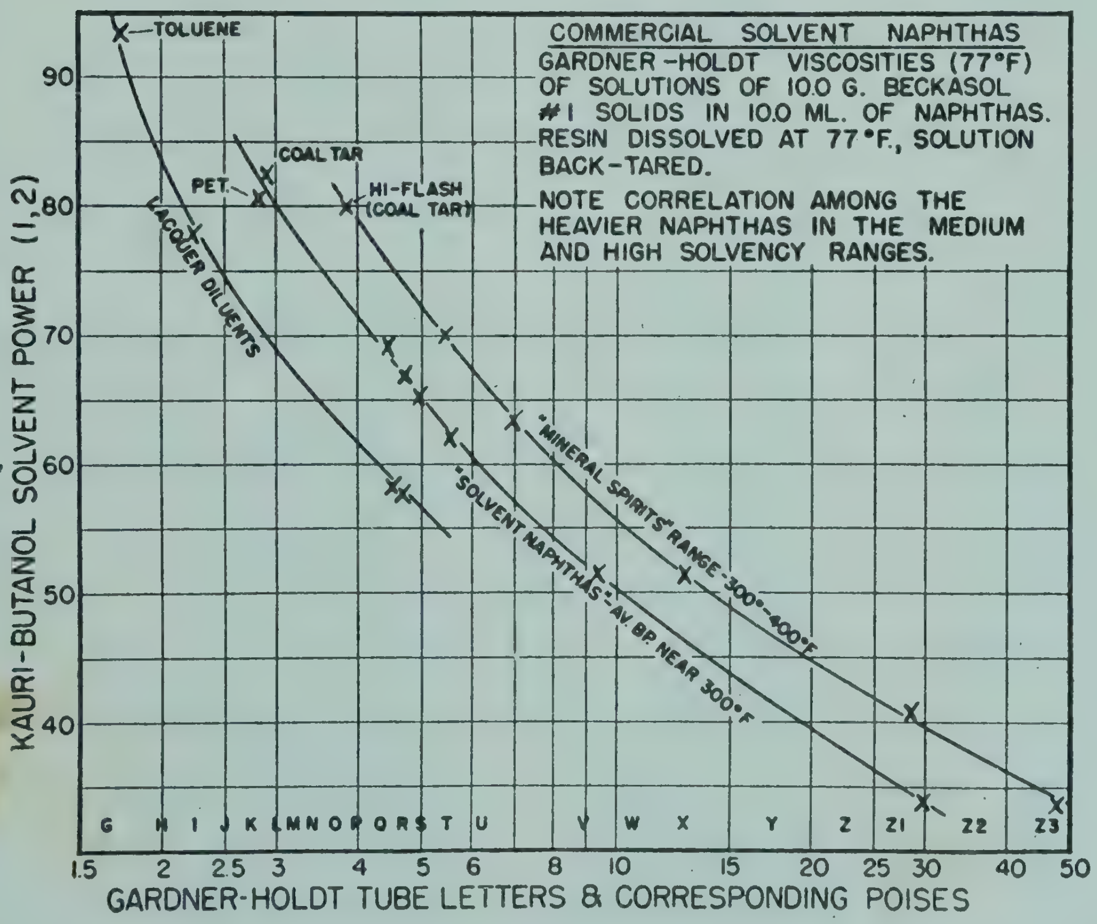

Figure 4.8.[8]

$[V]_P$ or $[V]_T$. If there is subtracted from either of these volumes the corresponding values for the limiting volume, there will be obtained the free volumes for isobar $[F]_P$ and isotherm $[F]_T$. The fluidities $[\varphi]_P$ and $[\varphi]_T$ are directly proportional to these free volumes.

Table 4.3. Viscosity (in Centipoises) of Various Substances*

Acetaldehyde	0.2234(19.2)
Acetamide	1.32(105)
Acetic anhydride	0.98(25)
Acetone	0.316(25)
Aceto-nitrile	0.34(25)
Acetylene dichloride	0.391(25)
Acetylene tetrachloride	1.637(25)
Allyl alcohol	1.283(22.8)
n-Amyl acetate	0.811(25)
n-Amyl alcohol	4.573(233)
sec-Amyl alcohol	3.10(25)
tert-Amyl alcohol	3.63(25)
Amyl butyrate	1.2558(25)
Amyl caproate	2.2707(25)
Amyl propionate	0.9355(25)
Amyl valerate	0.6227(25)
Aniline	3.70(25)
Benzaldehyde	1.40(25)
Benzene	0.60(25)
Benzonitrile	1.25(25)
Benzyl acetate	1.423(45)
Benzyl alcohol	5.054(25)
Benzylamine	1.59(25)
Benzyl benzoate	8.504(25)
Butyl acetate	0.6714(25)
n-Butyl alcohol	2.46(25)
tert-Butyl alcohol	5.887(22.41)
n-Butylamine	0.681(25)
Butyl caproate	1.348(25)
n-Butyl formate	0.5627(20)
Butyl valerate	1.348(25)
n-Butyric acid	1.599(20)
Carbon disulfide	0.35(20)
Carbon tetrachloride	0.88(25)
Chloroform	0.54(25)
Cyclohexanol	20.3(39.1)
Cyclohexanone	2.30(17.3)
Cyclopentanone	1.07(25)
Diethylamine	0.35(25)
Diethyl oxalate	1.76(25)
Diethyl phthalate	10.1(25)
Diethylene glycol	0.38(20)
Diphenyl ether	3.864(25)
n-Dipropyl ketone	0.685(25)
α-Epichlorhydrin	1.03(25)
Ethyl abietate	6.05(250)
Ethyl acetate	0.441(25)
Ethyl acetoacetate	1.53(25)
Ethyl alcohol	1.05(25)
Ethyl benzene	0.632(25)
Ethyl benzoate	2.14(25)
Ethyl bromide	0.3734(25.3)
Ethyl butyrate	0.63(25)
Ethyl caproate	0.9881(25)
Ethyl ether	0.223(25)
Ethyl formate	0.389(25)
Ethyl propionate	0.5045(25)
Ethyl salicylate	1.803(145)
Ethyl sebacate	5.1(25)
Ethyl stearate	3.75(50)
Ethyl valerate	0.7623(25)
Ethylene diamine	1.54(25)
Ethylene dibromide	1.698(20.6)
Ethylene glycol	17.4(25)
Ethylene trichloride	0.550(25)
Formanilide	8.70(55)
Formic acid	1.635(24.2)
Glycerol	8.3(20.3)
Isoamyl acetate	0.79(25)
Isoamyl alcohol	3.80(25)
Isoamylamine	0.7235(25)
Isoamyl ether	1.40(11)
Isoamyl formate	0.794(20)
Isobutyl alcohol	3.37(25)
Isobutyl butyrate	0.9766(25)
Isobutyl formate	0.6650(20)
Isobutyl propionate	0.67(25)
Isomethyl butyl ketone	0.5799(20)
Isopropyl acetate	0.5247(20)
Isopropyl alcohol	2.15(24.4)
Isopropyl formate	0.5134(20)
Mesityl oxide	0.879(25)
Methyl acetanilid	0.82(120)
Methyl acetate	0.3706(22.74)
Methyl acetoacetate	1.702(20)
Methyl alcohol	0.546(25)
n-Methyl amyl ketone	0.766(25)
Methyl benzoate	2.067(20)
n-Methyl butyl ketone	0.584(25)
Methyl *n*-butyrate	0.530(25)
Methyl isobutyrate	0.5170(20)
Methyl caproate	0.8096(25)
Methyl carbamate	2.28(55.6)
Methyl ethyl ketone	0.497(25)
Methyl formate	0.3298(25.5)
Methyl propionate	0.461(20)
n-Methyl propyl ketone	0.473(25)
Methyl valerate	0.6227(25)
Methylene chloride	0.4137(25.6)
Monobromobenzene	0.985(30)
Monochlorobenzene	1.03(0)
Nitrobenzene	2.013(20)
Pentachlorethane	2.26(25)
Phenetole	1.1158(25)
β-Phenyl ether alcohol	7.61(25)
Phenyl methyl ether	1.01(25)
n-Propyl acetate	0.551(25)
n-Propyl alcohol	1.91(25)
n-Propyl benzene	0.793(25)
n-Propyl butyrate	0.8296(20)
Propyl caproate	1.2864(25)
n-Propyl formate	0.5134(20)
n-Propyl propionate	0.6722(20)
Propyl valerate	0.6227(25)
Propylene dichloride	0.873(25)
Pyridine	0.88(25)
Tetrachloroethylene	0.838(25)
Tetralin 1,2,3,4	2.00(25)
Tetralin 5,6,7,8	2.00(25)
Toluene	0.552(25)
Trichloroethylene	0.550(25)
Triethylamine	0.363(25)
Turpentine (wood)	1.34(25)
m-Xylene	0.79(12)
o-Xylene	0.95(12)
p-Xylene	0.80(12)

* Figures in parentheses are temperature in °C.

Table 4.4. Viscosity at 25°C. of 5 Per Cent Solutions of Nitrocellulose[2]

Butyl Acetal By Vol.	Ethyl Acetate By Vol.	Ethyl Alchol By Vol.	Benzene By Vol.	Time of Flow Secs.	Time of Flow Secs.	Corrected Viscosity Glycerol = 100
100				71.4	71.4	43.1
90		10		31.6	31.3	18.9
90			10	75.0	75.0	43.3
80		20		24.6	24.2	14.6
80			20	87.0	87.0	52.5
60		40		21.5	20.6	12.4
60			40	36.2	35.8	21.6
40		60		20.0	20.7	12.5
40		30	30	25.8	25.0	15.1
20		80		24.1	22.2	13.4
20		10	70	53.0	47.0	28.4
	100			31.6	31.6	19.0
	90	10		23.4	23.1	13.9
	90		10	36.0	36.0	21.7
	80	20		17.2	16.8	10.5
	80	10	10	21.5	21.5	13.5
	80		20	40.8	40.8	24.7
	60	40		16.0	15.3	9.2
	60		40	64.6	64.4	38.9
	40	60		17.7	16.7	10.1
	40	30	30	19.4	18.8	11.4
	40		60	150.0	149.0	90.0
	20	80		22.8	20.8	12.6

Table 4.5. Viscosity of Nitrocellulose-Dammar Solutions[7]

Butyl Acetate %	Butyl Propionate %	Ethyl Acetate %	Toluene %	0.5-Sec. Cotton %	Dammar	Viscosity (Secs.)
	9.6	22.6	44.7	15.4	7.7	1.5
9.6		22.6	44.7	15.4	7.7	1.3
	7.4	25.8	46.0	15.8	5.0	1.2
7.4		25.8	46.0	15.8	5.0	1.4
	14.8	18.4	46.0	15.8	5.0	1.0
14.8		18.4	46.0	15.8	5.0	1.4
17.0		17.0	45.0	16.0	5.0	1.4
	10.0	24.0	45.0	16.0	5.0	1.4
24.0		10.0	45.0	16.0	5.0	1.8
	14.0	20.0	45.0	16.0	5.0	1.6

6. When mercury is subjected to pressure, the rheolar concentration, *i.e.*, the reciprocal of the molar free volume, is a linear function of the pressure. If 39,780 is added to the pressure in atmospheres, the rheolar concentration is directly proportional to the total pressure. This correction to the applied pressure of 39,780 atmospheres, is a measure of the internal pressure. For this quantity, Prof. T. W. Richard obtained the value of 41,300.

TABLE 4.6. SHRINKAGE FACTORS FOR VOLUME AND WEIGHT FRACTIONS AT VARIOUS TEMPERATURES[11]

Volume Fractions of A = Ethanol, B = Water at 60° F.		
f_A	ρ/ρ_B	ψ_A
1.00	0.79389	0.00000
0.90	0.83382	0.02147
0.80	0.86380	0.03586
0.70	0.88999	0.04895
0.60	0.91344	0.06184
0.50	0.93426	0.07463
0.40	0.95178	0.08556
0.32	0.96296	0.09036
0.30	0.96534	0.09058
0.28	0.96760	0.09039
0.20	0.97596	0.08591
0.10	0.98661	0.07221
0.05	0.99282	0.06251
0.02	0.99703	0.05761
0.00	1.00000	

Weight Fractions of A = Ethanol, B = Water at 10° C.		
F_A	ρ	Ψ_A
1.00	0.79784	0.00000
0.90	0.82654	0.02023
0.80	0.85197	0.03626
0.70	0.87602	0.05131
0.60	0.89927	0.06688
0.50	0.92162	0.08355
0.40	0.94238	0.10093
0.30	0.95977	0.11428
0.25	0.96665	0.11619
0.20	0.97252	0.11316
0.15	0.97800	0.10498
0.10	0.98393	0.09251
0.05	0.99098	0.07711
0.00	0.99973	

Weight Fractions of A = Ethanol, B = Water at 20° C.		
F_A	ρ	Ψ_A
1.00	0.78934	0.00000
0.92	0.81142	0.01556
0.90	0.81795	0.01978
0.80	0.84344	0.03530
0.70	0.86766	0.04974
0.60	0.89113	0.06444
0.50	0.91384	0.08009
0.40	0.93518	0.09626
0.30	0.95382	0.10961
0.24	0.96312	0.11294
0.20	0.96864	0.11206
0.10	0.98187	0.09821
0.05	0.98938	0.08591
0.02	0.99454	0.07861
0.00	0.99823	

Weight Fractions of A = Ethanol, B = Water at 30° C		
F_A	ρ	Ψ_A
1.00	0.78075	0.00000
0.90	0.80922	0.01935
0.80	0.83473	0.03442
0.70	0.85908	0.04834
0.60	0.88278	0.06240
0.50	0.90580	0.07716
0.40	0.92770	0.09250
0.30	0.94741	0.10591
0.25	0.95607	0.11004
0.20	0.96395	0.11118
0.15	0.97133	0.10861
0.10	0.97875	0.10278
0.05	0.98670	0.09368
0.00	0.99568	

Weight Fractions of A = Ethanol, B = Water at 40° C.		
F_A	ρ	Ψ_A
1.00	0.77203	0.00000
0.90	0.80028	0.01887
0.80	0.82578	0.03353
0.70	0.85025	0.04704
0.60	0.87417	0.06060
0.50	0.89750	0.07468
0.40	0.91992	0.08938
0.30	0.94055	0.10281
0.25	0.94991	0.10780
0.20	0.95856	0.11038
0.15	0.96670	0.10988
0.10	0.97475	0.10658
0.05	0.98311	0.10008
0.00	0.99225	

Weight Fractions of A = Ethanol, B = Water at 20° C.		
F_B	ρ	Ψ_B
1.00	0.99823	0.00000
0.90	0.98187	0.01091
0.80	0.96864	0.02802
0.70	0.95382	0.04698
0.60	0.93518	0.06417
0.50	0.91384	0.08009
0.40	0.89113	0.09667
0.30	0.86766	0.11606
0.20	0.84344	0.14119
0.10	0.81795	0.17799
0.05	0.80424	0.20429
0.00	0.78934	

Weight Fractions of A = Sulfuric Acid, B = Water at 20° C.		
F_A	ρ	Ψ_A
1.00	1.8305	0.0000
0.90	1.8144	0.0452
0.80	1.7272	0.0730
0.70	1.6105	0.0886
0.60	1.4983	0.1018
0.50	1.3951	0.1145
0.40	1.3028	0.1301
0.30	1.2185	0.1483
0.20	1.1394	0.1652
0.10	1.0661	0.1825
0.08	1.0522	0.1872
0.06	1.0385	0.1925
0.04	1.0250	0.1996
0.02	1.0118	0.2178
0.00	0.9982	

TABLE 4.7. SHRINKAGE FACTORS FOR VOLUME AND WEIGHT FRACTIONS AT VARIOUS TEMPERATURES[11]

Volume Fractions of A = Ethanol, B = Water at 60° F.

f_A	ρ/ρ_B	ψ_A
1.00	0.79389	0.00000
0.90	0.83382	0.02147
0.80	0.86380	0.03586
0.70	0.88999	0.04895
0.60	0.91344	0.06184
0.50	0.93426	0.07463
0.40	0.95178	0.08556
0.32	0.96296	0.09036
0.30	0.96534	0.09058
0.28	0.96760	0.09039
0.20	0.97596	0.08591
0.10	0.98661	0.07221
0.05	0.99282	0.06251
0.02	0.99703	0.05761
0.00	1.00000	

Weight Fractions of A = Ethanol, B = Water at 10° C.

F_A	ρ	Ψ_A
1.00	0.79784	0.00000
0.90	0.82654	0.02023
0.80	0.85197	0.03626
0.70	0.87602	0.05131
0.60	0.89927	0.06688
0.50	0.92162	0.08355
0.40	0.94238	0.10093
0.30	0.95977	0.11428
0.25	0.96665	0.11619
0.20	0.97252	0.11316
0.15	0.97800	0.10498
0.10	0.98393	0.09251
0.05	0.99098	0.07711
0.00	0.99973	

Weight Fractions of A = Ethanol, B = Water at 20° C.

F_A	ρ	Ψ_A
1.00	0.78934	0.00000
0.92	0.81142	0.01556
0.90	0.81795	0.01978
0.80	0.84344	0.03530
0.70	0.86766	0.04974
0.60	0.89113	0.06444
0.50	0.91384	0.08009
0.40	0.93518	0.09626
0.30	0.95382	0.10961
0.24	0.96312	0.11294
0.20	0.96864	0.11206
0.10	0.98187	0.09821
0.05	0.98938	0.08591
0.02	0.99454	0.07861
0.00	0.99823	

Weight Fractions of A = Ethanol, B = Water at 30° C

F_A	ρ	Ψ_A
1.00	0.78075	0.00000
0.90	0.80922	0.01935
0.80	0.83473	0.03442
0.70	0.85908	0.04834
0.60	0.88278	0.06240
0.50	0.90580	0.07716
0.40	0.92770	0.09250
0.30	0.94741	0.10591
0.25	0.95607	0.11004
0.20	0.96395	0.11118
0.15	0.97133	0.10861
0.10	0.97875	0.10278
0.05	0.98670	0.09368
0.00	0.99568	

Weight Fractions of A = Ethanol, B = Water at 40° C.

F_A	ρ	Ψ_A
1.00	0.77203	0.00000
0.90	0.80028	0.01887
0.80	0.82578	0.03353
0.70	0.85025	0.04704
0.60	0.87417	0.06060
0.50	0.89750	0.07468
0.40	0.91992	0.08938
0.30	0.94055	0.10281
0.25	0.94991	0.10780
0.20	0.95856	0.11038
0.15	0.96670	0.10988
0.10	0.97475	0.10658
0.05	0.98311	0.10008
0.00	0.99225	

Weight Fractions of A = Ethanol, B = Water at 20° C.

F_B	ρ	Ψ_B
1.00	0.99823	0.00000
0.90	0.98187	0.01091
0.80	0.96864	0.02802
0.70	0.95382	0.04698
0.60	0.93518	0.06417
0.50	0.91384	0.08009
0.40	0.89113	0.09667
0.30	0.86766	0.11606
0.20	0.84344	0.14119
0.10	0.81795	0.17799
0.05	0.80424	0.20429
0.00	0.78934	

Weight Fractions of A = Sulfuric Acid, B = Water at 20° C.

F_A	ρ	Ψ_A
1.00	1.8305	0.0000
0.90	1.8144	0.0452
0.80	1.7272	0.0730
0.70	1.6105	0.0886
0.60	1.4983	0.1018
0.50	1.3951	0.1145
0.40	1.3028	0.1301
0.30	1.2185	0.1483
0.20	1.1394	0.1652
0.10	1.0661	0.1825
0.08	1.0522	0.1872
0.06	1.0385	0.1925
0.04	1.0250	0.1996
0.02	1.0118	0.2178
0.00	0.9982	

ρ = density; number subscripts denote particular solutions and letter subscripts denote pure constituents

F = weight fraction; letter subscripts show particular constituents

f = volume fraction; letter subscripts show particular constituents

x = weight of solution taken

Ψ = shrinkage factor for weight fractions; letter subscript denotes constituent, the quantity of which is held constant

ψ = shrinkage factor for volume fractions; letter subscript denotes constituent, the quantity of which is held constant

7. On combining laws (6) and (4) which are the analogs of the laws of Boyle and Charles, there results the more general law that

$$\frac{(P + 39{,}780)}{t + 272.8} F = R_{\mathrm{L}} = 0.1069 \text{ liter–atm.}$$

It is therefore possible to calculate the fluidity of mercury at any temperature and pressure by first reducing the volume to the standard condition of 0° and 760 mm pressure and then applying law (5). This equation is being worked out for polyatomic molecules."[10]

When liquids are mixed to form a solution, changes in volume will take place, and these changes are commonly shrinkages. Parsons and Estrada[11] have devised a simple and convenient method of calculating the shrinkage or expansion of solutions after mixing. This is accomplished by finding the "shrinkage factor" from the composition of the solution, its density, and the density of the component parts. They have also uncovered such little-known facts as, for example, that the dilution of certain concentrations of ethyl alcohol will cause expansion instead of contraction of volume. This is also true of methyl, *n*-propyl, and isopropyl alcohols.

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Chapter 5

The Industrial Applications of Solvents

The amazing growth of the solvents industry can be fairly comprehended when we realize that from a few solvents, such as the aliphatic and aromatic hydrocarbons, methyl and ethyl alcohols, acetone, glycerin and turpentine, has grown a giant industry producing over five hundred different solvents. As shown in Table 5.1, these are derived from a variety of natural raw materials and include about a half dozen principal types. One of the fastest growing segments of the solvents industry is the aliphatic chemical or *petrochemicals* branch. McClure and Bateman[1] have pointed out the remarkable growth of this industry over the past 20 years, both from the standpoint of tonnage and diversity of products. This is clearly shown in Figs. 5.1 and 5.2, indicating a total U. S. production of nearly 9 billion pounds of synthetic aliphatics alone.

Ewell[2] has indicated the effect of the progress of chemical technology on the manufacture of certain industrial solvents. For example, prior to 1924, acetone was produced exclusively from hardwood distillation or by fermentation, whereas by 1944 about 85 per cent was obtained via isopropanol. In the case of butanol, the fermentation product accounted for all the output in 1924, but only 33 per cent by 1944, the balance being synthetic butanol made from acetaldehyde. This is illustrated by Boruff and Van Lanen[3] in Fig. 5.3 showing the proportions of the output of butanol and acetone provided by synthetic and fermentative processes.

The economic interrelationships of the various processes utilized commercially for the production of aliphatic solvents are graphically coordinated in Fig. 5.4 taken from the work of Ewell[2].

Many other solvents are at present produced only on a moderate scale, or are undergoing commercial development, but these are finding wider application every day, and are carrying, and may carry, many as yet unknown or unheralded solvents in their wake.

The modern solvent industry produces many billions of pounds of solvents annually in the United States. These are no longer limited to the old industrial standbys, such as paint, varnish and lacquer, but have branched out until they are now essential in such diversified industries as:

(a) Industrial coatings
(b) Antifreeze
(c) Brake fluids

TABLE 5.1. PRINCIPAL TYPES OF INDUSTRIAL SOLVENTS AND THEIR SOURCES

- Coal
  - Alcohols
  - Carbon disulfide
  - Chlorinated hydrocarbons
  - *Coal Tar*
    - Benzol
    - Toluol
    - Xylol
    - Naphthas
    - Phenols
    - Naphthalene
- Petroleum
  - VMP Naphtha
  - Stoddard solvent
  - Mineral spirits
  - *Aromatics*
    - Toluol
    - Cyclohexane
  - Aliphatic *Hydrocarbons*
    - Alcohols
    - Ethers
    - Esters
    - Ketones
    - Chlorinated Hydrocarbons
    - Glycol ethers
    - Nitroparaffins
  - *Fluorinated Solvents*
    - "Freons"
    - "Genetrons"
- Molasses, *Grains*
  - Alcohols
  - Esters
  - Ketones
- Hydrogenated *Solvents*
  - Cyclohexanol
  - Cyclohexanone
  - "Tetralin"
- *Corn Cobs*
  - Furfural
  - Furfuryl Alcohol
- Wood
  - *Pine*
    - Turpentine
    - Terpene solvents
  - *Hardwood*
    - Methanol

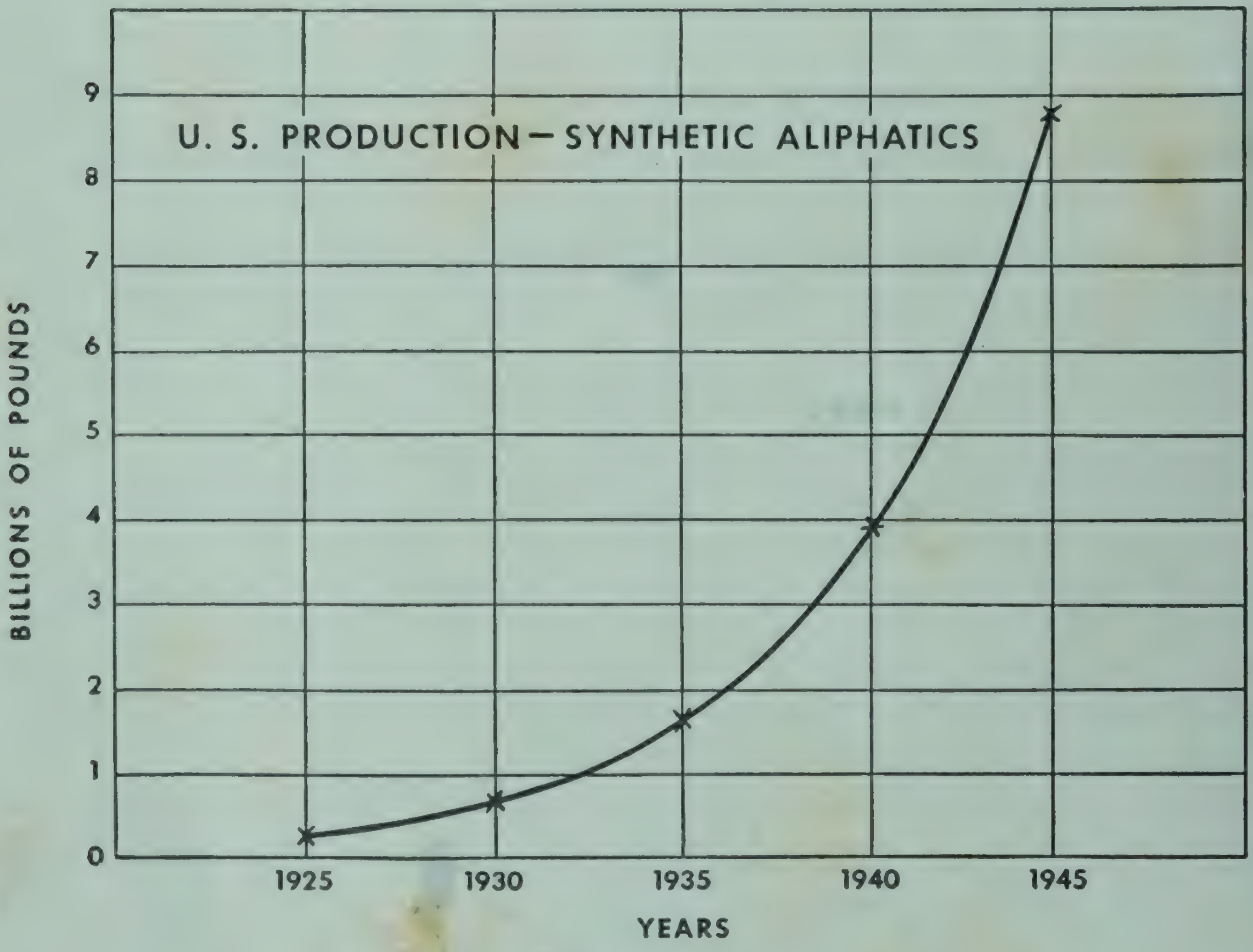


Figure 5.1.[1]

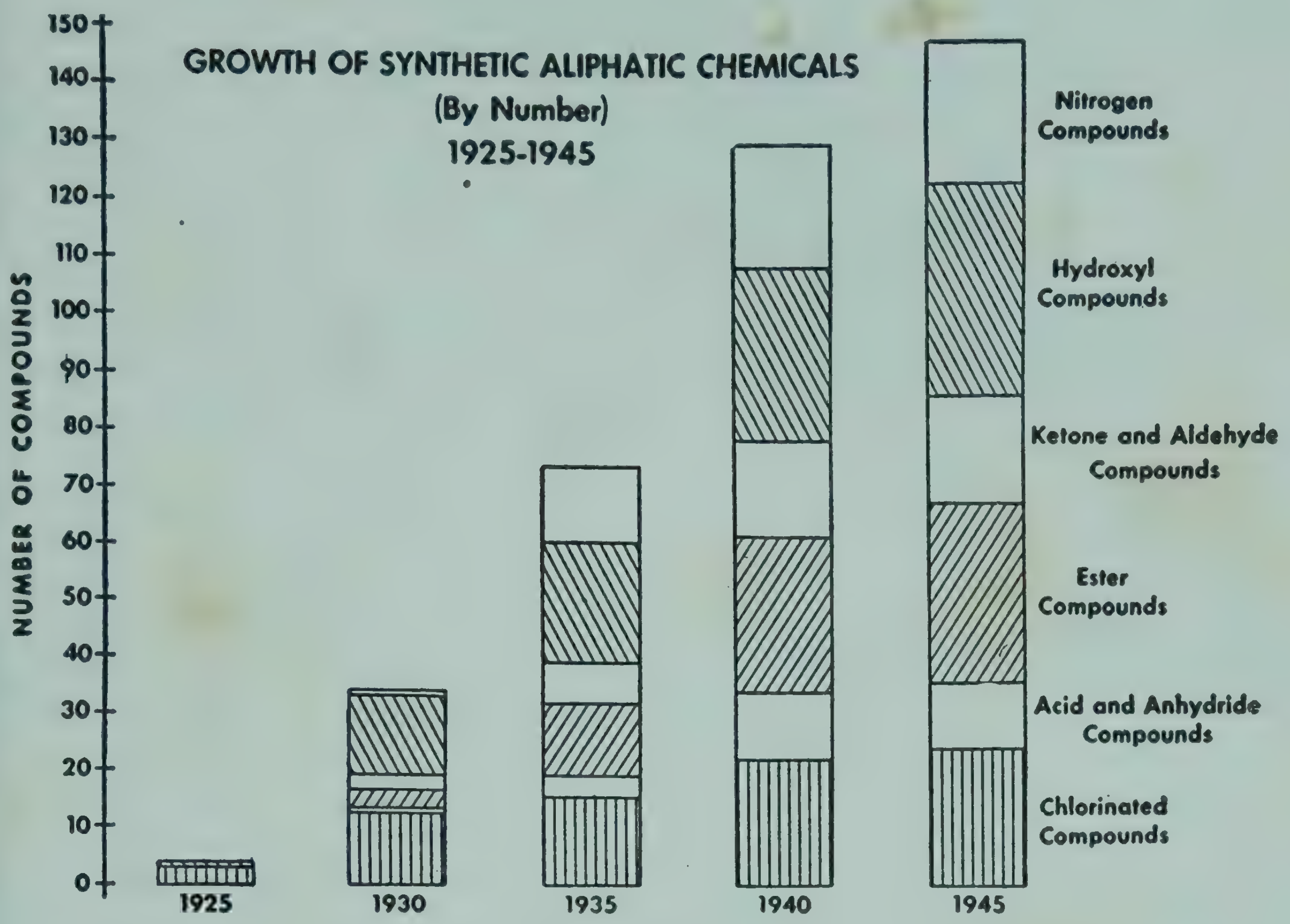


Figure 5.2.[1]

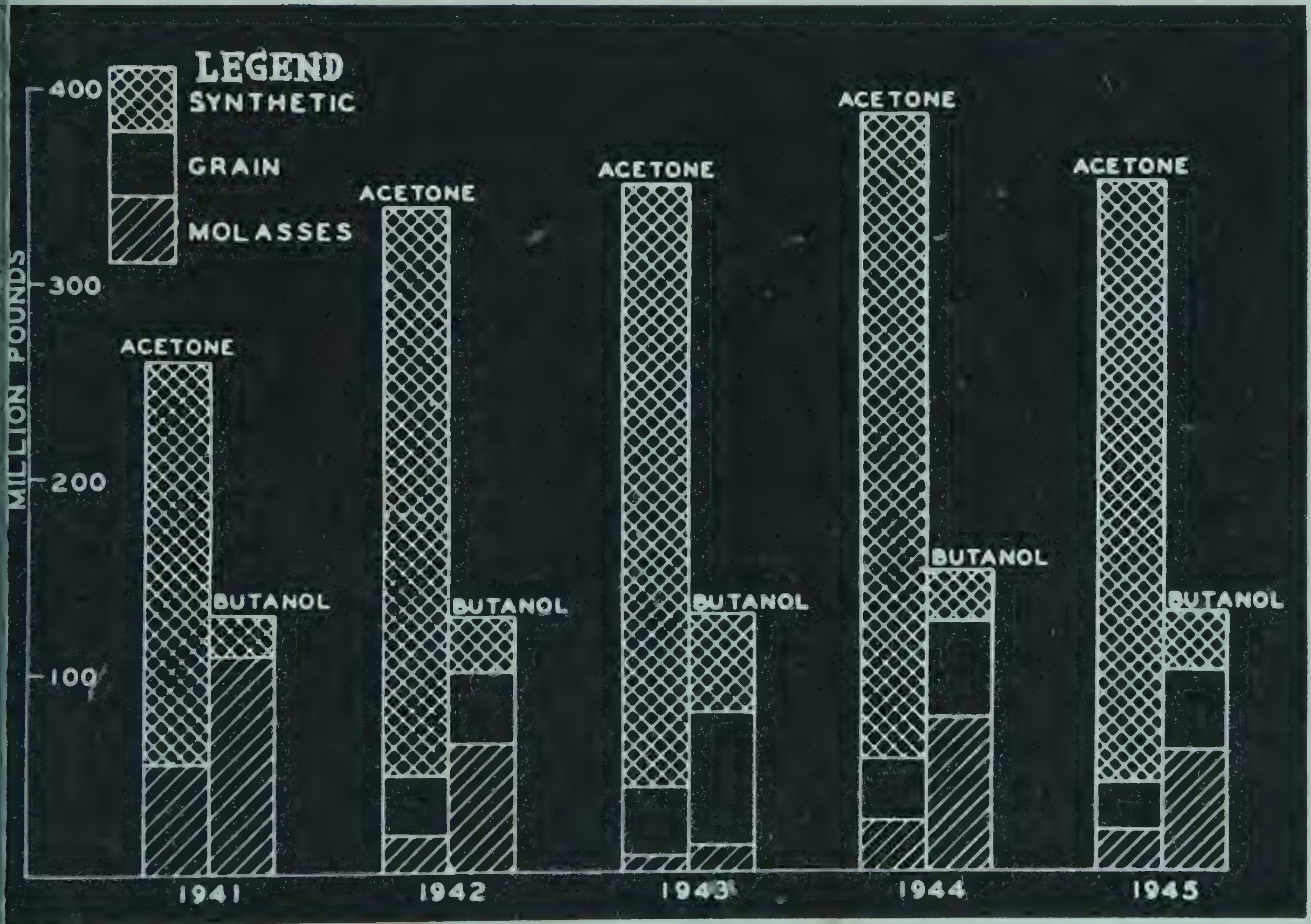
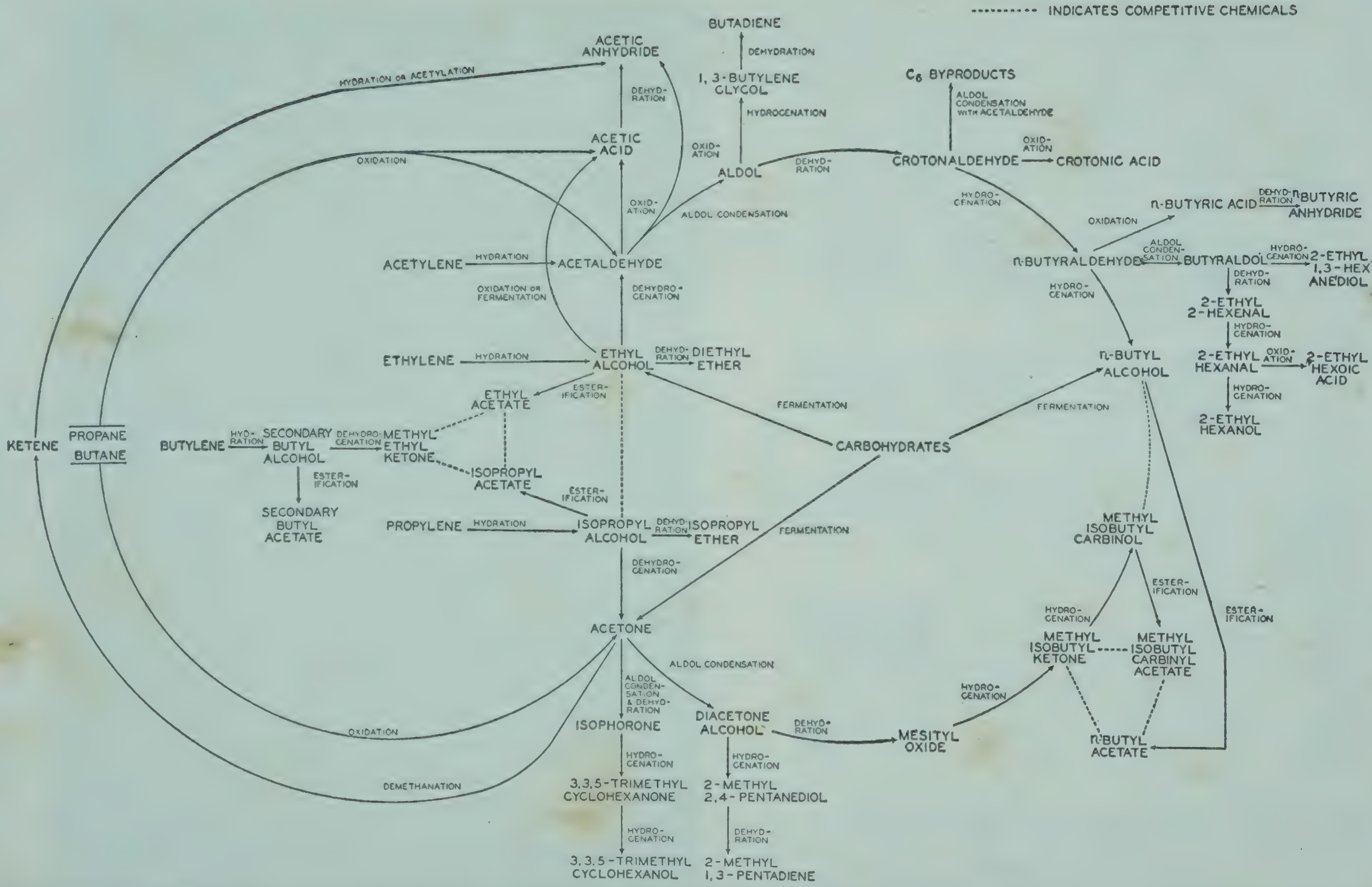


Figure 5.3.[3]



--------- INDICATES COMPETITIVE CHEMICALS
ACETIC ANHYDRIDE
HYDRATION OR ACETYLATION
DEHYDRATION
ACETIC ACID
OXIDATION
OXIDATION
BUTADIENE
DEHYDRATION
1, 3-BUTYLENE GLYCOL
HYDROGENATION
OXIDATION
ALDOL
ALDOL CONDENSATION
DEHYDRATION
C$_6$ BYPRODUCTS
ALDOL CONDENSATION WITH ACETALDEHYDE
CROTONALDEHYDE
OXIDATION
CROTONIC ACID
HYDROGENATION
n-BUTYRIC ACID
DEHYDRATION
n-BUTYRIC ANHYDRIDE
OXIDATION
n-BUTYRALDEHYDE
ALDOL CONDENSATION
BUTYRALDOL
HYDROGENATION
2-ETHYL 1,3-HEXANEDIOL
DEHYDRATION
2-ETHYL 2-HEXENAL
HYDROGENATION
2-ETHYL HEXANAL
OXIDATION
2-ETHYL HEXOIC ACID
HYDROGENATION
2-ETHYL HEXANOL
HYDROGENATION
n-BUTYL ALCOHOL
ACETYLENE
HYDRATION
ACETALDEHYDE
OXIDATION OR FERMENTATION
DEHYDROGENATION
ETHYLENE
HYDRATION
ETHYL ALCOHOL
DEHYDRATION
DIETHYL ETHER
ESTERIFICATION
ETHYL ACETATE
FERMENTATION
FERMENTATION
CARBOHYDRATES
KETENE
PROPANE
BUTANE
BUTYLENE
HYDRATION
SECONDARY BUTYL ALCOHOL
DEHYDROGENATION
METHYL ETHYL KETONE
ESTERIFICATION
SECONDARY BUTYL ACETATE
ISOPROPYL ACETATE
ESTERIFICATION
PROPYLENE
HYDRATION
ISOPROPYL ALCOHOL
DEHYDRATION
ISOPROPYL ETHER
FERMENTATION
DEHYDROGENATION
ACETONE
ALDOL CONDENSATION
ALDOL CONDENSATION & DEHYDRATION
ISOPHORONE
HYDROGENATION
3,3,5-TRIMETHYL CYCLOHEXANONE
HYDROGENATION
3,3,5-TRIMETHYL CYCLOHEXANOL
DIACETONE ALCOHOL
HYDROGENATION
2-METHYL 2,4-PENTANEDIOL
DEHYDRATION
2-METHYL 1,3-PENTADIENE
DEHYDRATION
MESITYL OXIDE
HYDROGENATION
METHYL ISOBUTYL KETONE
HYDROGENATION
METHYL ISOBUTYL CARBINOL
ESTERIFICATION
METHYL ISOBUTYL CARBINYL ACETATE
ESTERIFICATION
n-BUTYL ACETATE
OXIDATION
DEMETHANATION

Figure 5.4. Economic Interrelationships of Unit Processes.[2]

(d) Vegetable oil extraction
(e) Lube oil refining
(f) Dry cleaning
(g) Insecticides
(h) Rayon manufacture

Some idea of the variety of industrial applications may be gained by reference to Table 5.2. The protective-coatings industry continues to claim one of the top places as an outlet for solvents.

Industrial Coatings[5]

The principal solvents and thinners consumed in the manufacture of paint and varnish products are petroleum products, turpentine, alcohols, esters, ketones, and coal-tar derivatives, in the average proportions indicated in the automobile lacquer formulation below.

According to one authority[6], an estimated 71,000,000 gallons of solvents and thinners were required in 1939 in the manufacture of paint and varnish products and another 19,000,000 gallons were required for final application of those products by painters and private individuals. The total estimated consumption of solvents in that year for paint and varnish products, therefore, amounted to about 90,000,000 gallons. In addition to this amount, about 29,000,000 gallons of solvents and thinners were used in the manufacture and application of nitrocellulose lacquer, making a total of about 119,000,000 gallons of solvents and thinners.

Lacquer solvents are so blended that the mixture will dissolve cellulose derivatives, natural and synthetic resins and wet pigments; and so that it will be stable, prevent blush, and give any desirable evaporation rate. Solvency is increased by mixing solvents or adding certain ones that possess more than one dissolving group in the molecule. This increased solvent power allows for the addition of diluents and nonsolvents, and thus anticipates the never-ceasing demands for lower-cost lacquers. Ethyl acetate is in a class by itself owing to the fact that the lower-boiling solvents, such as acetone and methyl acetate, are much too volatile. The higher esters are used admixed with ethyl acetate and usually constitute the main portion of the solvent mixture. Other good solvents are the secondary esters and the "Cellosolve" glycol ether compounds. The latter, however, are distinguished by their ability to tolerate fairly large quantities of coal-tar diluents. Lacquer diluents should have a distillation range and an evaporation rate very similar to those of the main solvent in the solvent mixture; they should also be free of corrosive material, should leave no residue, and should possess solvent power. Thinners for interior gloss paint and enamel should be completely volatile and free of sulfur. It has been pointed out that enamel discoloration is owing to a reaction between sulfur and the constituents of the enamel.

TABLE 5.2. THE USE OF SOLVENTS IN INDUSTRY[4]

INDUSTRY							
Automotive and Aircraft	Chemical Process	Food Industries	Pharmaceutical and Medicinal	Plastics and Rubber	Surface Coatings	Soaps, Cosmetics	Textile and Leather
Alcohols							
Anti-freeze, lacquer solvents, brake fluids	Preparation of esters, ethers, acids, aldehydes, solvents, extractants	Extracts, flavors	Preparation of medicinals, tinctures, extracts, manufacture of hypnotics	Formaldehyde manufacture—process solvents, wetting nitrocellulose	Solvents for stains, lacquers, shellac, varnishes, resins	Soap solvents perfumes, toiletries, extraction of perfumes	Solvent in printing, manufacture of rayon, dyeing
Glycols							
High-temperature coolants, safety glass, brake fluids, anti-freeze	Manufacture of explosives, natural gas, dehydration	Flavors	Vehicles, extractants	Manufacture of resins and plasticizing	Stains, solvent for gums, plasticizers	Perfume solvents, coupling agents, mutual solvents	Dye solvents, printing pastes, conditioners
Alcohol-ethers							
Safety glass, brake fluid	Synthesis	Package sealing	Vehicles, extractants	Process solvents	Solvents in lacquers, varnishes, stains	Cleaning compounds, emolients, couplers	Dye solvents

				Esters			
Lacquer solvents and plasticizers	Ethylation, dye synthesis	Flavor synthesis, package coating solvents	Manufacture of antipyretics, analgesics	Manufacture of film, rayon, cellulose derivatives	Lacquers, varnishes, dopes, inks, plasticizers	Manufacture of perfumes, fixatives	Lacquer solvents, acetic acid concentration
				Acids and Anhydrides			
Cellulose esters for safety glass, dopes	Synthesis	Synthesis of flavors	Manufacture of aspirin and drugs	Cellulose acetate, safety film	Cellulose ester lacquers	Essential oil synthesis	Synthesis dyes and rayon
				Ethers and oxides			
Manufacture of lube oils	Extractants, solvents, synthesis	Fumigants	Special ointments	Nitrocellulose solvents	Varnish removers, lacquer solvents	Synthetic detergents, essential oil manufacture	Spotting, scouring, dye solvents
				Aldehydes			
	Synthesis acids, alcohols, nitriles	Flavor synthesis	Synthesis	Synthetic resins and rubber accelerators	Resin synthesis	Preparation of essential oils	Synthesis dyes and tanning compounds

TABLE 5.2—*Continued*

INDUSTRY							
Automotive and Aircraft	Chemical Process	Food Industries	Pharmaceutical and Medicinal	Plastics and Rubber	Surface Coatings	Soaps, Cosmetics	Textile and Leather
Ketones							
Dewaxing oils, dope solvents	Synthesis	Package coating solvents	Extraction of drugs and capsule cleaning	Artificial leather, film, pyroxylin manufacture	Lacquers, dopes, paint removers, vinyl resins	Essential oil synthesis	Manufacture of rayon
Chlorinated compounds							
Dewaxing oils, metal degreasing anti-knock compounds	Extraction of fats, oils, waxes, drugs	Fumigation, refrigeration	Vitamin concentration, extraction drugs	Solvents, manufacture of synthetic resins	Lacquer diluents, rubber cements	Cleaning and scouring compounds	Spotting, degumming
Amines							
Corrosion inhibitors, cutting oils Gas purification	Synthesis	Insecticides Herbicides	Synthesis, anesthetics, analgesics	Accelerators, anti-oxidants	Softening, moistening, plasticizing	Manufacture of soaps for emulsion, detergents	Scouring, dyeing, emulsifying, auxilliaries

Coal-tar solvents, such as toluene, xylene, and "Hi-Flash" naphtha, are solvents for alkyd resins and chlorinated rubber ("Tornesit" type), each of which is used to make corrosion-resistant finishes. They are also added to petroleum naphthas to fortify the solvency of the latter. These solvents will also dissolve rubber resins of the "Pliolite" type, polymerized cashew shell oil, synthetic drying oils like the divinyl acetylene polymers, and the coumarone and indene resins. Coal-tar solvents are employed in the making of gilsonite wood stains, as dispersion media for aluminum stearate, as flatting agents, for the removal of water from carbon black prior to grinding, and as thinners and dispersion agents for aluminum paints. Toluene and xylene substitutes are usually petroleum products extracted from asphaltic crudes or made by the hydrogenation of cracked petroleum products.

The work of Hofmann and Reid[8] is of special interest to those who wish to apply brushing lacquers to surfaces already coated with varnishes or enamels.

These workers have made the following general conclusions based on lifting tests:

"(a) The various single solvents (and diluents) may be arranged as below in order of increasing lifting tendency:

1. Petroleum hydrocarbons
2. Coal-tar hydrocarbons
3. Alcohols
4. Esters and glycol ethers

(b) Mixtures of two liquids in order of increasing lifting tendency:

1. Petroleum hydrocarbon + alcohol
2. Petroleum hydrocarbon + glycol ether
3. Coal-tar hydrocarbon + ester
4. Ester + alcohol
5. Coal-tar hydrocarbon + alcohol

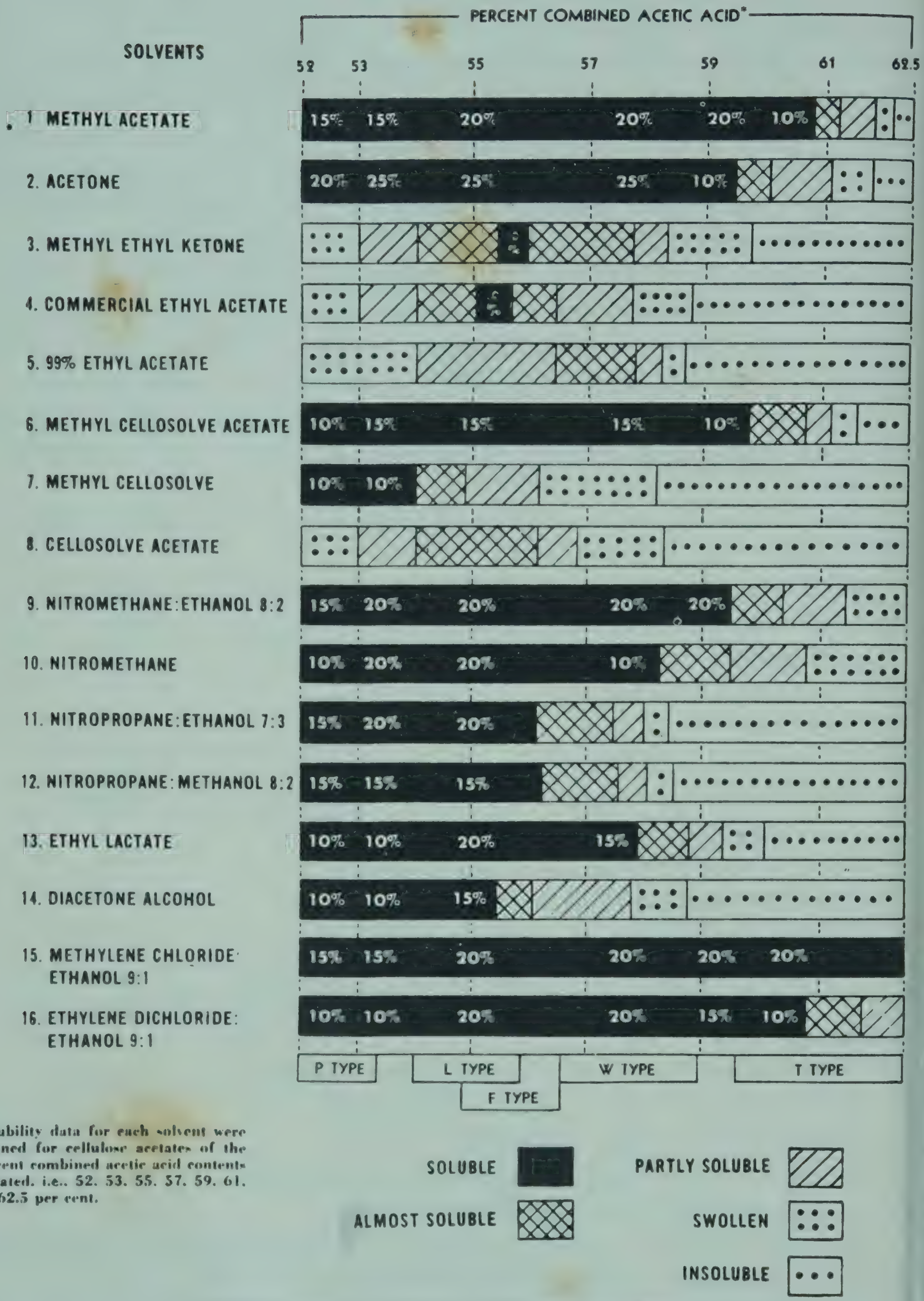
(c) Typical three-component mixtures listed in order of increasing lifting tendency:

1. Petroleum + alcohol + glycol ether solvent
2. Petroleum + ester + glycol ether solvent
3. Petroleum + ester + alcohol
4. Coal-tar hydrocarbon + alcohol + glycol ether
5. Coal-tar hydrocarbon + alcohol + ester

(d) Other things being equal—that is, in homologous series— the lifting tendency increases with increasing boiling point."

The higher-boiling esters and the glycol ethers have found a new application in the making of nonaqueous wood stains. The light-colored finishes of the vinyl derivative type are soluble in ketones and esters.

Other important industrial coating resins in use at the present time



Solubility data for each solvent were obtained for cellulose acetates of the per cent combined acetic acid contents indicated, i.e., 52, 53, 55, 57, 59, 61, and 62.5 per cent.

Percentage figures in solid areas show maximum solubility concentrations of cellulose acetate at 25°C.

Figure 5.5. Solubility of Low-Viscosity Cellulose Acetate.[6]

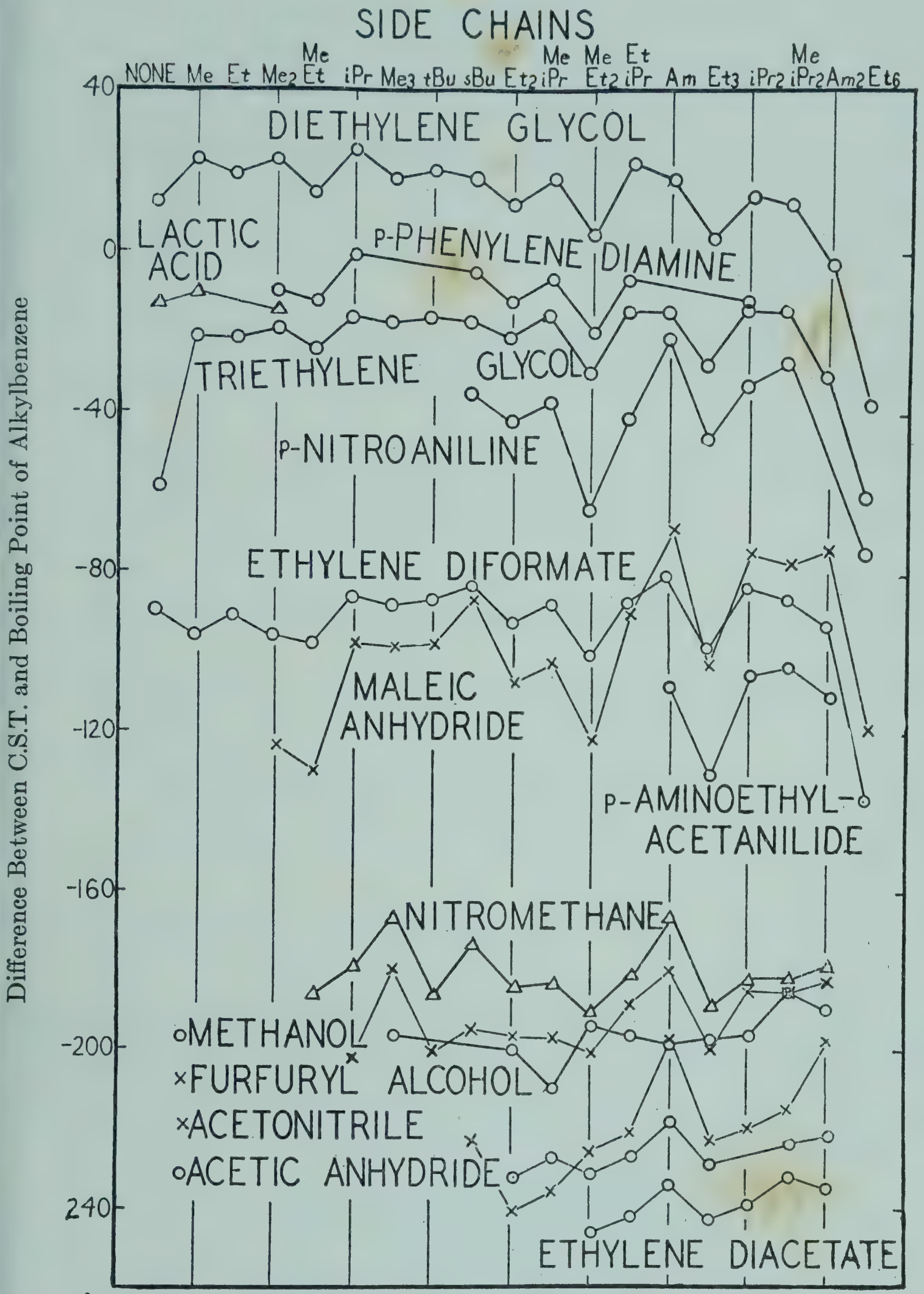


Figure 5.6. Relation of Critical Solution Temperature to Boiling Point of Alkylbenzenes.

include the following types: cellulose acetate, cellulose acetobutyrate, acrylates, vinyl resins, and ethyl cellulose. The large number of useful solvents and solvent combinations available commercially for cellulose acetate and vinyl resins are shown in the tables which follow.

TABLE 5.3. LIFTING OF VARNISHES[8]*

	Varnish No.**																							
	1		2		3		4		5		6		7		8		9		10		11		12	
	Age, Days																							
Solvent	16	99	16	99	16	99	16	99	16	99	16	99	16	99	16	99	16	99	16	99	16	99	16	99
⅔ Toluene ⅓ Butanol	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	0	0	0	0	x	x
⅔ Toluene ⅓ Butyl acetate	0	x	x	x	x	0	x	x	0	0	x	x	0	0	x	x	x	x	0	0	0	0	x	0
⅔ Kemsolene ⅓ Butanol	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
⅔ Kemsolene ⅓ Butyl acetate	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	x	0	0	0	0	0	0	0
½ Butyl acetate ½ Butanol	0	0	x	0	x	x	x	x	x	x	x	x	x	x	x	x	x	x	0	0	0	0	x	x
½ Ethyl acetate ½ 95% Alcohol	0	0	0	0	x	x	0	0	0	x	0	0	x	0	0	0	0	x	0	0	0	0	x	x
⅔ Toluene ⅓ "Cellosolve"	0	x	x	0	x	x	x	x	x	0	x	x	x	0	x	0	x	x	0	0	0	0	x	x
⅔ Toluene ⅓ C.S. acetate	0	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	0	0	0	0	x	x
⅔ Denat. alcohol ⅓ "Cellosolve"	0	0	0	0	x	x	0	0	x	0	0	0	x	x	x	0	0	0	0	0	0	0	x	x
⅔ Denat. alcohol ⅓ C.S. acetate	0	0	0	0	x	x	0	0	x	x	0	0	x	x	x	0	0	x	0	0	0	0	x	x
50% Toluene 20% Butanol 30% Butyl acetate	x	0	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	0	0	0	0	x	x
50% Kemsolene-T 20% Denat. alcohol 30% "Cellosolve"	0	0	0	0	x	x	0	0	x	x	0	x	0	x	x	0	x	x	0	0	0	0	x	x
70% Toluene 15% Ethyl acetate 15% "Cellosolve"	0	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	0	0	0	0	x	x
40% Kemsolene-T 20% Denat. alcohol 20% Ethyl acetate 20% Butyl "Cellosolve"	0	0	0	0	0	0	0	0	0	x	0	x	0	0	0	0	x	0	0	0	0	0	x	x
70% Toluene 15% Ethyl acetate 15% C.S. acetate	0	0	x	0	0	0	x	0	0	0	x	x	0	0	x	x	x	x	0	0	0	0	0	0

1. 10-gallon linseed oil—Kauri gum varnish
2. 10-gallon tung oil—Kauri gum varnish
3. 20-gallon linseed oil—Ester gum[a] varnish
4. 20-gallon tung oil—Ester gum varnish
5. 35-gallon linseed oil—Ester gum[a] varnish
6. 35-gallon tung oil—Ester gum[b] varnish
7. 60-gallon linseed oil—Ester gum[a] varnish
8. Same as (3), without driers
9. Same as (4), without driers
10. 20-gallon tung oil—zinc hardened rosin varnish
11. Long oil white enamel, zinc oxide pigment
12. Long oil enamel vehicle, without pigment

[a] These varnishes were made by mixing a heavy kettle-bodied linseed oil with an Ester gum solution and an appropriate quantity of lead and manganese linoleate driers.

[b] Contained a small amount of free rosin.

*X = Lifted.   0 = Did not lift.

**Varnishes used in Lifting Tests.

TABLE 5.4. INFLUENCE OF THINNERS ON DURABILITY[9]

Paint Designation	Ratio of Lead to Zinc	Comparison Group[a]	Thinner	Weight of Panel[b] Grams	Range of Angle of Grain[c] Degrees	Side Painted[d]	Weight of Paint Applied[e] Lb./100 sq. ft.[i]	Durability Based on Integrity Weeks	Order of Merit[f]	Moisture Fluctuation[g] Grams	End Checks[h] Inches (cm.)
			Paints Applied to White Pine								
C1	60 : 30	1	Steam-distilled wood turpentine	341	2–3	B	5.47	21	3	220	1 (2.5)
			Mineral spirits (brand H)	350	0–2	B	5.35	21	1	248	0
			Mineral spirits (brand H)	355	2	B	5.35	21	2	243	0
		2	Gum turpentine	365	5–24	B	5.29	18	2	265	0
			Mineral spirits (brand W)	360	6–24	B	5.65	>21[j]	1	168	0
		3	Steam-distilled wood turpentine	344	16–50	B	5.47	>21	2	135	0
			Destructively distilled wood turpentine	334	19–46	B	5.35	>21	1	132	0
C2	60 : 30	4	Gum turpentine	379	3–17	B	5.29	21	3	183	0
			Gum turpentine	381	6–18	B	5.29	21	2	182	0
			Steam-distilled wood turpentine	374	14–21	B	5.59	>21	1	184	0
			Steam-distilled wood turpentine	382	8–14	B	5.59	21	2	180	4 (10.2)
		5	Destructively distilled wood turpentine	370	19	P	5.11	>21	1	131	0
			Mineral spirits (brand W)	362	16–20	P	5.17	>21	2	148	0
		6	Mineral spirits (brand H)	355	37–62	P	4.99	>21	2	125	0
			Mixture of gum turpentine and H	349	25–57	B	6.20	>21	1	122	0
		7	Destructively distilled wood turpentine	349	56–69	P	5.11	>21	1	124	0
			Mineral spirits (brand W)	341	37–66	B	5.17	>21	2	131	0
D2	75 : 25	8	Gum turpentine	330	4–9	B	6.25	>21	1	104	2 (5.1)
			Mineral spirits (brand W)	345	5–21	B	5.54	20	2	202	2 (5.1)
N	Lithopone-zinc	9	Gum turpentine	327	11–14	P	Not determined	>21	1	114	0
			Steam-distilled wood turpentine	322	2–14	P		>21	2	122	0
			Mineral spirits (brand W)	323	5–13	P		20	3	246	0
		10	Destructively distilled wood turpentine	397	6–26	B	Not determined	>21	1	42	0
			Mineral spirits (brand H)	404	0–18	B		20	2	169	0
		11	Steam-distilled wood turpentine	360	25–45	P	Not determined	>21	2	90	0
			Mineral spirits (brand W)	361	42–55	P		>21	3	92	5 (12.7)
			Mixture of gum turpentine and H	361	30–53	P		>21	1	101	0
C1		12	Mineral spirits (brand W)	366	20–21	P	5.65	>21	1	132	0
C2			Mineral spirits (brand W)	362	16–20	P	5.17	>21	2	148	0
C1	60 : 30	13	Destructively distilled wood turpentine	334	19–46	B	5.35	>21	2	132	0
C2			Destructively distilled wood turpentine	349	56–69	P	5.11	>21	1	124	0
C1		14	Mixture of gum turpentine and H	330	7–15	P	5.59	>21	2	132	0
C2			Mixture of gum turpentine and H	349	5–10	B	6.20	>21	1	220	2 (5.1)

TABLE 5.4. INFLUENCE OF THINNERS ON DURABILITY—*Continued*

Paint Designation	Ratio of Lead to Zinc	Comparison Group[a]	Thinner	Weight of Panel[b] *Grams*	Range of Angle of Grain[c] *Degrees*	Side Painted[d]	Weight of Paint Applied[e] *Lb./100 sq. ft.*[i]	Durability Based on Integrity *Weeks*	Order of Merit[f]	Moisture Fluctuation[g] *Grams*	End Checks[h] *Inches (cm.)*
			Paints Applied to Yellow Pine								
White Lead		15	Destructively distilled wood turpentine	543	50–82	B	7.50	21	3	228	0
			Steam-distilled wood turpentine	542	69–81	B	7.74	>21	2	139	0
			Gum turpentine	605	70–78	B	8.28	>21	1	85	0
			Oxidized turpentine	542	76–80	B	7.47	>21	2	99	0
			Mineral spirits (Midcontinent)	522	49–64	B	7.49	21	2	112	0
			Varnish and paint makers' naphtha	516	59–68	P	7.73	>21	1	99	0
			Mineral spirits (Pa.)	505	34–44	B	7.53	21	2	224	0
			Solvent naphtha	509	40–64	B	7.11	>21	3	165	0
			Mineral spirits (Calif.)	506	30–45	B	7.40	>21	2	191	1 (2.5)
			Mineral spirits (Mexico)	501	46–51	B	7.00	>21	3	193	0
White lead		16	Destructively distilled wood turpentine	667	27–43	P	7.50	21	1	295	4 (10.2)
			Steam-distilled wood turpentine	671	30–67	P	7.74	21	1	290	5 (12.7
			Gum turpentine	631	27–52	P	8.28	21	1	345	4 (10.2)
			Oxidized turpentine	641	9–46	P	7.47	21	2	445	4 (10.2)
			Mineral spirits (Midcontinent)	640	14–43	P	7.49	21	5	526	13 (33)
			Varnish and paint makers' naphtha	641	18–37	P	7.73	21	4	528	19 (48)
			Mineral spirits (Pa.)	631	11–26	B	7.53	18	2	570	23 (58)
			Solvent naphtha	616	19–30	P	7.11	21	3	559	26 (66)
			Mineral spirits (Calif.)	624	19–24	P	7.40	21	3	582	21 (53)
			Mineral spirits (Mexico)	601	34–37	P	7.00	21	2	550	18 (46)
Lead-zinc	45 : 40	17	Destructively distilled wood turpentine	564	67–69	B	5.25	20	1	276	0
			Steam-distilled wood turpentine	602	58–68	B	5.75	20	2	200	0
			Gum turpentine	605	65–78	B	5.09	20	4	228	0
			Oxidized turpentine	595	67–80	B	5.31	20	1	320	1 (2.5)
			Mineral spirits (Midcontinent)	609	80–85	B	4.91	18	3	280	16 (41)
			Varnish and paint makers' naphtha	588	76–78	P	4.54	18	3	282	15 (38)
			Mineral spirits (Pa.)	612	72–73	B	4.96	18	3	308	12 (31)
			Solvent naphtha	608	72–75	B	4.62	18	3	284	12 (31)
			Mineral spirits (Calif.)	625	62–74	P	4.74	18	3	238	1 (2.5)
			Mineral spirits (Mexico)	675	43–69	B	4.52	14	2	217	2 (5.1)
Lead-zinc	45 : 40	18	Destructively distilled wood turpentine	640	47–70	P	5.25	14	1	89	0
			Steam-distilled wood turpentine	618	34–36	B	5.75	20	3	120	0
			Gum turpentine	590	27–29	B	5.09	20	1	89	2 (5.1)
			Oxidized turpentine	580	50–69	P	5.31	20	1	99	0
			Mineral spirits (Midcontinent)	597	28–65	B	4.91	18	4	99	0
			Varnish and paint makers' naphtha	599	80–83	P	4.54	20	1	111	0
			Mineral spirits (Pa.)	591	64–69	P	4.96	20	2	79	0
			Solvent naphtha	621	79–84	P	4.62	>20	5	101	0
			Mineral spirits (Calif.)	618	69–88	B	4.74	20	1	88	3 (7.6)
			Mineral spirits (Mexico)	579	61–89	B	4.52	18	2	110	0

[a] Each comparison group consisted of panels cut from same long board.

[b] Determined when all panels were of approximately same moisture content.

[c] Angle at which annual rings reached painted surface of panel.

[d] Pitch (P) or bark (B) side.

[e] Average for each group of panels receiving same paint and hence not rigidly applicable to individual panel.

[f] Order of integrity at end of test, value 1 representing best integrity.

[g] Summation of ten fluctuations.

[h] Found to influence moisture-fluctuation values.

[i] One pound per 100 square feet equals 4.9 kg. per 10 square meters.

[j] Greater than 21 weeks; *i. e.*, still sound at end of test.

TABLE 5.5. EFFECT OF DIFFERENT THINNERS ON THE DURABILITY OF PAINT

Paint and Thinner	At Madison, Wis.				At Washington, D. C.				At Gainesville, Fla.			
		Durability				Durability				Durability		
	Wt. of pigment[a]	Integrity	Protection and integrity	Order of merit at end	Wt. of pigment[a]	Integrity	Protection and integrity	Order of merit at end	Wt. of pigment[a]	Integrity	Protection and integrity	Order of merit at end
	Lbs./100 sq. ft.	*Months*			*Lbs./100 sq. ft.*	*Months*			*Lbs./100 sq. ft.*	*Months*		
Paste Paint:												
Turpentine, gum spirits	6.99	22	21	4	6.88	15	13	3	7.08	15	12	5
Turpentine, steam-distilled	7.05	27	23	2	7.57	18	13	2	7.09	15	6	5
Turpentine, destructively distilled	7.43	30	30	2	7.18	18	13	2	7.49	15	12	5
Turpentine, oxidized	7.29	30	24	1	7.54	24	18	1	8.20	35	18	1
Mineral spirits from Pennsylvania crude oil	7.17	24	23	3	6.92	15	13	5	8.37	23	12	3
Mineral spirits from Midcontinent crude oil	7.48	26	23	3	7.47	15	13	4	7.99	18	9	5
Mineral spirits from California crude oil	7.15	26	24	3	6.50	18	11	4	6.67	23	12	3
Mineral spirits from Mexican crude oil	8.08	30	27	1	8.05	18	11	3	8.08	23	12	2
Painters' naphtha from Midcontinent crude oil	7.18	28	26	2	8.14	22	13	3	8.38	23	12	2
Solvent naphtha from coal-tar	7.07	31	28	2	7.36	18	13	4	7.89	15	3	4
Prepared Paint:												
Turpentine, gum spirits	5.23	15	15	3	5.73	13	13	2	4.80	15	15	4
Turpentine, steam-distilled	4.61	14	14	4	5.53	13	13	2	4.99	15	15	2
Turpentine, destructively distilled	4.48	15	15	4	4.64	13	13	2	4.04	15	15	2
Turpentine, oxidized	5.05	16	16	1	5.22	13	13	2	5.17	15	15	1
Mineral spirits from Pennsylvania crude oil	5.02	16	16	3	5.74	13	13	1	4.81	15	15	4
Mineral spirits from Midcontinent crude oil	4.84	16	16	3	4.65	13	13	2	4.05	15	15	5
Mineral spirits from California crude oil	4.53	15	15	5	4.61	13	13	2	4.65	15	15	3
Mineral spirits from Mexican crude oil	4.57	15	15	6	4.73	13	13	1	4.45	15	15	3
Painter's naphtha from Midcontinent crude oil	5.15	16	16	2	5.05	13	13	1	5.12	15	15	3
Solvent naphtha from coal tar	5.60	16	16	2	5.11	13	13	1	5.13	15	15	3

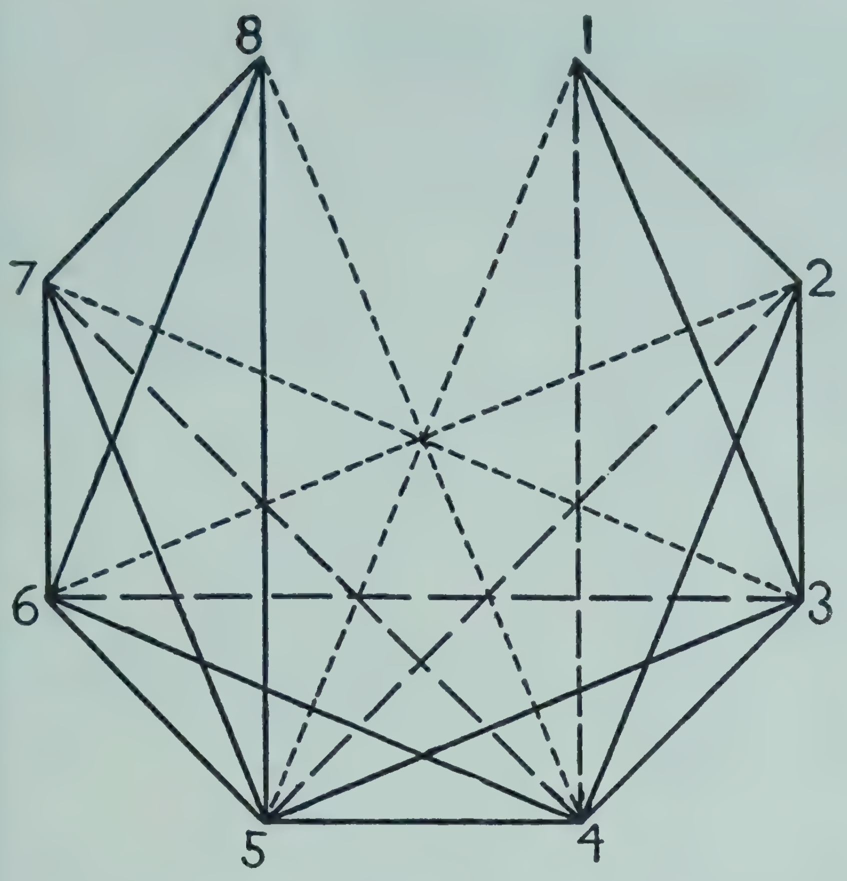
TABLE 5.5. EFFECT OF DIFFERENT THINNERS ON DURABILITY OF PAINT—*Continued*

Paint and Thinner	At Fresno, Calif.				At Pittsburgh, Pa.				Weighted Average for All Stations (c)			
		Durability				Durability				Durability		
	Wt. of pigment[a]	Integrity	Protection and integrity	Order of merit at end	Wt. of pigment[a]	Integrity[b]	Protection and integrity[b]	Order of merit at end[b]	Wt. of pigment[a]	Integrity	Protection and integrity	Order of merit at end
	Lbs./100 sq. ft.	*Months*			*Lbs./100 sq. ft.*	*Months*			*Lbs./100 sq. ft.*	*Months*		
Paste Paint:												
Turpentine, gum spirits	6.61	19	19	3	8.28	41	41	1	7.09	21.1	19.9	7
Turpentine, steam-distilled	6.80	19	19	3	7.74	41	41	1	7.23	22.8	18.9	5
Turpentine, destructively distilled	7.50	19	19	2	7.50	41	41	1	7.41	23.4	21.7	4
Turpentine, oxidized	7.78	22	22	1	7.47	41	41	1	7.68	29.6	23.5	1
Mineral spirits from Pennsylvania crude oil	7.02	19	3	4	7.53	41	41	1	7.40	23.2	16.8	7
Mineral spirits from Midcontinent crude oil	7.47	19	19	4	7.49	41	41	1	7.60	22.5	19.6	8
Mineral spirits from California crude oil	7.68	19	3	3	7.40	41	41	1	7.08	24.2	16.6	6
Mineral spirts from Mexican crude oil	7.14	19	3	2	7.00	41	41	1	7.73	25.2	17.2	2
Painters' naphtha from Midcontinent crude oil	7.00	19	19	3	7.73	41	41	1	7.69	25.6	20.7	3
Solvent naphtha from coal-tar	7.04	19	19	2	7.11	41	41	1	7.32	23.6	19.4	5
Prepared Paint:												
Turpentine, gum spirits	4.79	11	11	2	5.09	29	29	2	5.13	15.6	15.6	6
Turpentine, steam-distilled	5.12	17	17	2	5.75	26	26	3	5.16	16.3	16.3	5
Turpentine, destructively distilled	4.72	6	6	2	5.25	35	35	1	4.58	15.4	15.4	3
Turpentine, oxidized	4.83	17	17	2	5.31	29	29	2	5.10	17.2	17.2	1
Mineral spirits from Pennsylvania crude oil	5.06	17	17	2	4.96	26	26	3	5.12	16.7	16.7	5
Mineral spirits from Midcontinent crude oil	4.61	17	17	2	4.91	26	26	4	4.58	16.7	16.7	9
Mineral spirts from California crude oil	4.97	19	19	1	4.74	26	26	5	4.82	16.9	16.9	8
Mineral spirits from Mexican crude oil	4.73	17	17	2	4.52	28	28	2	4.60	16.8	16.8	7
Painters' naphtha from Midcontinent crude oil	5.15	19	19	2	4.54	26	26	2	5.03	17.1	17.1	2
Solvent naphtha from coal-tar	4.99	17	17	2	4.62	26	26	5	5.12	16.7	16.7	4

[a] One pound per 100 square feet equals 4.9 kg. per 10 sq. m.

[b] All panels with paste paint at Pittsburgh were still rated "good" in integrity and protection when last inspected, which was 35 months after exposure. The durability was therefore arbitrarily set at 41 months and they were all given the merit rating 1.

[c] In computing the weighted averages the Pittsburgh station was given a weight of two-thirds because the sets of panels were made from two boards instead of three.



1. Water
2. Diethylene glycol
3. Triethylene glycol
4. Furfural
5. Ethyl ether
6. Benzene
7. Cyclohexane
8. *n*-Heptane

Figure 5.7. Mutual Solubility of liquids
———— Complete miscibility
— — — — High solubility
- - - - - - - Low solubility
No line Very low solubility

Table 5.6. Indication of the Solubility* of the More Usual Resins[10]

Rosin Thus Elemi Mastic	soluble in	Esters (more readily soluble in esters than in alcohol) Alcohols Hydrocarbons Ketones
Dammar Ester gum Cumar	soluble in	Esters Hydrocarbons Alcohols + hydrocarbons or esters
	partly soluble in	Alcohols Ketones
Shellac Sandarac	soluble in	Alcohols Alcohols + esters Ketones (solubility varies with grade of resin)
	insoluble in	Esters Hydrocarbons
Kauri Pontianac Soft manilas	soluble in	Alcohols Alcohols + esters (more soluble than in alcohol alone) Alcohols + hydrocarbons
	partly soluble in	Ketones
	insoluble in	Esters Hydrocarbons
Hard manilas Congo Benguela Angola Madagascar Zanzibar	partly soluble in	Alcohols Alcohols + esters (esters must be in small amount)
	insoluble in	Esters Hydrocarbons Ketones

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*The word "soluble" in this classification means that 95 per cent by weight or more of the resin was soluble in the solvent. Some resins—for example, shellac—have a waxy residue if not "refined." This residue is not considered as part of the resin in this solubility classification.

TABLE 5.7. SOLVENTS USEFUL WITH CELLULOSE ACETATE[6]

SOLVENT	W. LBS./ GALLON	BOILING POINT °C	VOLATILITY*	VISCOSITY† AT 25 °C
Methylene chloride	11.4	42	1.8	Nonsolvent alone (see alcohol mixture below
Methanol	6.6	64.7	6.3	Cosolvent
Acetone	6.6	56.5	2.1	46 (see mixtures below)
Methyl acetate	7.55	57.2	2.2	62
Methyl ethyl ketone	6.7	79.6	2.4	203*
Ethyl acetate (85%)	7.2	77.1	2.9	151*
Ethanol	6.6	78.4	7.0	Cosolvent
Ethylene dichloride	10.45	83.7	4.1	Cosolvent
Dioxan	8.5	101.4		308
Nitromethane	9.5	101	5.8	207 (see mixtures below)
Toluene	7.2	109.5–110.5	6.1	Diluent
beta-Trichloroethane	12.0	113	4.5	Cosolvent
1-Nitropropane	8.4	132	8.0	Cosolvent
Methyl cellosolve	8.0	121–126	34.5	360‡
Methyl cellosolve acetate	8.4	143–145	35	350
Ethyl lactate	8.6	119–176	80	720
Diacetone alcohol	7.8	153–160	147	650
Carbitol acetate	8.4	211–220	150+	Solvent only when hot

SOLVENT MIXTURES	VISCOSITY	SOLVENT MIXTURES	VISCOSITY
9 Methylene chloride:1 Ethanol	84	8 Nitromethane:2 Ethanol	109
9 Ethylene dichloride:1 Ethanol	200	7 Nitromethane:3 Ethanol	102
8 Ethylene dichloride:2 Ethanol	137	8 *1*-Nitropropane:2 Ethanol	185
9 Acetone:1 Ethanol	42	9 Methyl ethyl ketone:1 Methanol	62
9 Acetone:1 Methanol	40	8 Methyl ethyl ketone:2 Methanol	70
9 Nitromethane:1 Ethanol	120	86 Methyl ethyl ketone:14 Methanol	80

* Based on Gardner's ratings, "Paints, Varnishes, Lacquers & Colors," p. 1082 (1937 ed.).

† Rated from centipoise viscosity of 9% LL-1 cellulose acetate solutions in solvents shown.

‡ These solutions were shaken overnight, heated 2 hrs. at 65°C, then cooled overnight to measurement temperature.

The commercial products made from acrylic derivatives vary widely in their solubilities, as evidenced by the fact that the various grades are supplied as solutions in a large assortment of solvents such as toluene, ethyl acetate, "Cellosolve" acetate and ethylene dichloride.

Some very important and fundamental information regarding the action of solvents on chlorinated rubber has been contributed by Raynolds, Rad-

TABLE 5.8. Quantitative* Solubilities of "Vinylite" Resin Vyhh in Various Solvent-Diluent Mixtures[4]

SOLVENT-DILUENT	MAXIMUM % RESIN VYHH SOLUBLE IN SOLVENT-DILUENT MIXTURE INDICATED WITHOUT THIXOTROPISM AT 20°C		MAXIMUM % RESIN VYHH SOLUBLE IN 50% SOLVENT–50% DILUENT MIXTURE WITHOUT GELATION AT 20°C	VISCOSITY, IN CENTIPOISES, 15% RESIN VYHH IN 50% SOLVENT–50% DILUENT MIXTURE AT 20°C
	15% Solvent, 85% Diluent	50% Solvent, 50% Diluent		
	A	*B*	*C*	*D*
Acetone-Toluene	11.5	18.6	30.0	31
Methyl Ethyl Ketone-Toluene	9.5	17.5	29.8	39
Methyl Ethyl Ketone-"Troluoil"	insol.	10.0	10.0	10 (10% solution)
Methyl n-Propyl Ketone-Toluene	10.4	16.6	27.5	50
Methyl Isobutyl Ketone-Toluene (10°C.)	6.1	13.8	21.2	82
Methyl Isobutyl Ketone-Toluene	8.3	16.0	22.0	76
Methyl Isobutyl Ketone-Toluene (30°C.)	9.0	18.8	29	50
Methyl Isobutyl Ketone-"Solvesso" No. 1†	insol.	14.5	21.0	67
Methyl Isobutyl Ketone-"Troluoil"	insol.	insol.	insol.	—
Methyl Isobutyl Ketone-monochlorotoluene	7.0	11.0	23.0	115
Mesityl Oxide-Toluene	9.0	17.0	27.8	64
Methyl n-Butyl Ketone-Toluene	10.5	16.8	22.8	65
Methyl n-Amyl Ketone-Toluene	7.6	16.4	20.0	93
Methyl n-Amyl Ketone-"Troluoil"	insol.	insol.	insol.	—
Methyl n-Amyl Ketone-Xylene	3.0	14.2	20.0	105
Methyl n-Amyl Ketone-"Tetralin"	11.5 (without gelation)	—	22.5	187
Methyl n-Hexyl Ketone-Toluene	6.7	14.5	18.3	120
Cyclohexanone-Toluene	11.5	20.5	35.0	80
Methyl Cyclohexanone-Toluene	17.0 (without gelation)	—	32.5	—
Isophorone-Xylene	12.0	19.0	33.2	145
Acetonylacetone-Toluene	11.0	16.0	31.0	108
Ethyl Acetate (99.3%)-Toluene	7.0	14.0	15.8	110

TABLE 5.8. QUANTITATIVE* SOLUBILITIES OF "VINYLITE" RESIN VYHH IN VARIOUS SOLVENT-DILUENT MIXTURES[4]—*Continued*

SOLVENT-DILUENT	MAXIMUM % RESIN VYHH SOLUBLE IN SOLVENT-DILUENT MIXTURE INDICATED WITHOUT THIXOTROPISM AT 20°C		MAXIMUM % RESIN VYHH SOLUBLE IN 50% SOLVENT–50% DILUENT MIXTURE WITHOUT GELATION AT 20°C	VISCOSITY, IN CENTIPOISES, 15% RESIN VYHH IN 50% SOLVENT–50% DILUENT MIXTURE AT 20°C
	15% Solvent, 85% Diluent	50% Solvent, 50% Diluent		
	A	*B*	*C*	*D*
n-Butyl Acetate (99.3%)-Toluene	insol.	12.0	13.9	gel
Nitroethane-Toluene	9.8	20.6	27.2	85
1-Nitropropane-Toluene	9.8	19.6	27.8	92
Methyl Isobutyl Ketone-Toluene	11.6	19.8	25.5	37

* Slight variations in commercial grades of materials involved will cause corresponding changes in the values.

† High aromatic grade (about 90%) was used in these tests. Lower aromatic grades will require more active solvent for equivalent results.

NOTE: It is customary to prepare base solutions, semi-pastes, and finished coatings containing concentrations of resin approximately 2 to 5 per cent lower than the values given in column "C" above in the thinner mixture indicated. This is in general entirely practical because normal room temperatures are higher than the 20°C (68°F) temperature at which this data was obtained. Also a slight amount of thioxotropism in the solutions eliminates much of the settling usually encountered in other types of pigmented materials.

TABLE 5.9. DILUTION RATIOS OF SOLVENTS FOR RUBBER CHLORIDE

SOLVENT	LACTOL SPIRITS DILUTION RATIO	SOLVENT	LACTOL SPIRITS DILUTION RATIO
"Solvesso No. 3"	0.08	Butyl lactate	2.09
Dipentene	0.10	Butyl propionate	2.12
"Solvesso No. 1"	0.12	Di-*n*-propyl ketone	2.22
"Solvesso No. 2"	0.23	Octyl acetate	2.30
Carbon tetrachloride	0.23	Amyl acetate	2.31
Hi-Flash solvent naphtha	0.26	*sec*-Butyl acetate	2.33
Xylene	0.38	Ethyl acetate	2.49
"Solvesso No. 4"	0.41	Methyl ethyl ketone	2.50
Benzene	0.49	Isobutyl acetate	2.59
Toluene	0.50	Isopropyl acetate	2.62
Dioxane	0.70	Methyl isobutyl ketone	2.67
Ethylene dichloride	0.81	Cyclohexyl acetate	2.80
Cyclohexanone	1.64	*n*-Butyl acetate	2.88

TABLE 5.10. Tolerance Ratios of Diluents and Rubber Chloride

DILUENT	TOLERANCE RATIO FOR 10% RAOLIN A IN BUTYL ACETATE	% BUTYL ACETATE IN 75% TOLERANT SOLUTION
Ethyl alcohol	0.33	80
Amyl alcohol	0.84	62
Butyl alcohol	0.86	61
Naphtha (Amsco)	2.15	38
Textile spirits	2.40	36
Kerosene	2.70	33
"Kemsolene T"	2.77	33
Lactol spirits	2.88	32
Gasoline (lead-free)	3.17	30
V. M. & P. naphtha	3.20	29
Acetone	3.90	25
"Sunoco" spirits	4.20	24
Mineral spirits	4.72	22

cliffe, and Vogel.[12] As a result of their studies a correlation has been made of the solvent action of a number of solvents and of the tolerance ratio for diluents.

Vegetable Oil Extraction

"Quite a number (20 or more) of solvents have been proposed for the commercial extraction of fats and oils. Among these may be mentioned the specially prepared solvent extraction gasoline or benzine, benzene (benzol) and various chlorinated products such as di- and trichloroethylene. Carbon disulfide has been extensively used for extracting the residual oil from olive press cake. Gasoline, on account of its cheapness and because it extracts less coloring matter and other non-oil constituents than most if not all other solvents, is in more general use, particularly for the extraction of oils intended for edible purposes, in which it is essential that all traces of the solvent be removed. The gasoline (benzine) employed for solvent extraction usually distills completely within a range of 20°C. Depending somewhat upon the type of the plant and also upon its location (temperate or tropical regions) the solvent used may distill from 60° to 80°, 80° to 100°, or 90° to 110° C. In comparing the costs, the density of the solvent should be given consideration, as a given weight of meal requires a definite volume of solvent for the recovery of the oil, and in contrast to gasoline most of the other solvents are much heavier than water. Although highly inflammable, gasoline is not subject to spontaneous combustion and there is practically no danger in its use in properly designed and operated extraction plants. On the other hand, the chlorinated solvents burn with difficulty. Carbon tetrachloride is not a satisfactory solvent because it undergoes some hydrolysis, resulting in the corrosion of the equipment. Di- and trichloroethylene are very stable solvents, but it is exceedingly important that they should under no circumstances be heated in the presence of any free alkali. Failure to observe this precaution has resulted in several explosions which were believed due to the formation of chloroacetylene by the action of caustic soda during the distillation of the solvent."[13]

During the period 1938 to 1942 when the importation of tung oil had practically ceased, the domestic crop became the important source of its supply and the drying-oil industry therefore bent every effort toward obtaining the maximum yield of tung oil from it. Freeman, Pack, and McKinney,[14] who contributed much to the solution of this problem, studied the effect of solvent extraction on tung oil by evaluating a wide variety of commercially available solvents and, at the same time, taking into consideration boiling points, solubility, stability, and reactivity. In this work 33 solvents were employed, the results tabulated as shown in Table 5.11.

One of the remarkable feats of selective solvent refining has been accomplished by Kaiser and Hancock,[16] who invented a process for refining wood rosin by two immiscible liquids at one time. The color components are dissolved by furfural and wood rosin is dissolved by petroleum ether. With this method a wood rosin is produced that is as pure as gum rosin. Furfural is not the only solvent which can do this. Humphrey [17] has shown that a correlation exists between the molecular structure of some organic compounds and their capacity to remove the color components of wood rosin, and he makes the following generalizations.

"I. Molecular simplicity is favorable, the lower members of a homologous series being superior to the higher. Methanol is superior to ethanol; ordinary phenol to the cresols; aniline to methylaniline; furfural to methylfurfural; methyl acetate to ethyl acetate, etc.

"II. Cyclic structure promotes refining. Alcohols, esters, ethers, and aldehydes having a cyclic group normally are better than simple aliphatics carrying the same group. Thus, furfural is greatly superior to acetaldehyde.

"The simple furan derivatives are usually more effective than their more or less analogous benzene counterparts. Furfural exerts more refining action than benzaldehyde; likewise, furfuryl ethers and furoic acid esters, such as methyl furoate, than the corresponding benzene derivatives.

"III. Unsaturation in the molecule may be helpful. Ordinary phenol is far superior to cyclohexanol, and furfuryl alcohol to tetrahydrofurfuryl alcohol.

"IV. Various substituents are essential, both for promotion of immiscibility of the two phases, as well as for specific solvent action on the com-

(Text continued on page 140)

TABLE 5.11. RESULTS OF EXTRACTING TUNG OIL FROM PREPARED KERNELS WITH VARIOUS SOLVENTS[a] [14]

	Solvent	Extraction Data			Check Extn. with Skellysolve F			Characteristics of Oil
		% oil	Iodine No., Wijs	$n_D^{27.5}$	% oil	Iodine No., Wijs	$n_D^{27.5}$	
1.	Isopentane, *P*	60.85	166.8	1.5178	63.25	167.0	1.5175	*A, G*
2.	*n*-Pentane, *P*	62.03	166.7	1.5175	63.25	167.0	1.5175	*A, G*
3.	Petroleum naphtha (pentanes-hexanes fraction), *N*	60.37	163.4	1.5162	59.57	165.1	1.5162	*A, G*
4.	Petroleum naphtha (pentanes-hexanes fraction), *N*	...	...	....	...	...	....	(From Skellysolve F, used as standard)
5.	Petroleum naphtha (mixed hexanes), *P*	62.15	166.6	1.5173	63.25	167.0	1.5175	*A, G*
6.	Petroleum naphtha (essentially *n*-hexane), *N*	61.65	159.3	1.5145	59.57	165.1	1.5162	*B, G*
7.	Petroleum naphtha (essentially *n*-hexane fraction), *N*	63.81	163.8	1.5161	61.97	164.9	1.5166	*B, G*
8.	Cyclohexane, *P*	64.24	162.6	1.5160	61.69	166.7	1.5172	*A, H*
9.	Benzene, *M*	62.18	160.2	1.5161	59.57	164.0	1.5162	*B, G*
10.	Benzene, *P*	64.74	161.8	1.5163	61.97	164.9	1.5166	*B, G*
11.	Petroleum naphtha (essentially *n*-heptane fraction), *N*	64.04	162.6	1.5159	61.97	164.9	1.5166	*C, J*
12.	Petroleum naphtha (essentially an octanes fraction), *N*	64.75	118.7	....	62.98	163.4	....	*B, K*
	Same	71.33	159.6	1.5150	69.41	163.8	1.5170	*B, R*
13.	Petroleum naphtha (essentially an octanes fraction), *N*	62.81	156.0	1.5134	59.57	165.1	1.5162	*C, J*
14.	Methylcyclohexane, *P*	64.79	162.6	1.5150	61.69	166.7	1.5172	*A, I*
15.	Methylcyclohexane, *N*	...	...	....	...	...	....	
16.	Toluene, *M*	65.46	161.8	1.5163	61.69	166.7	1.5172	*C, H*
17.	Petroleum naphtha (essentially high-boiling octanes fraction), *N*	63.73	149.6	1.5159	59.57	165.1	1.5162	*B, G*
18.	Xylene, *M*	68.96	150.4	1.5126	61.69	166.7	1.5172	*C, H*
19.	Methylene chloride, *P*	64.45	162.1	1.5169	63.25	167.0	1.5175	*A, G*
20.	*sym-trans*-Dichloroethylene, *P*	65.80	161.6	1.5154	64.03	162.2	1.5152	*A, G*
21.	Chloroform, *M*	66.08	164.3	1.5171	61.69	166.7	1.5172	*B, G*
22.	1,2-Dichloropropane, *P*	...	...	....	...	...	....	
23.	Carbon tetrachloride, *M*	66.69	156.9	1.5154	61.69	166.7	1.5172	*A, G*
24.	*n*-Butyl chloride, *P*	65.01	155.1	1.5150	63.25	167.0	1.5172	*A, G*
25.	Ethylene dichloride, *P*	68.06	155.3	1.5140	64.03	162.2	1.5152	*E, L, G*
26.	Trichloroethylene, *P*	...	...	....	...	...	....	
27.	Trichloroethylene, *P*	63.41	152.5	1.5145	64.03	162.2	1.5152	*F, I*
28.	1,1,2-Trichloroethane, *P*	...	...	....	...	...	....	
29.	Perchloroethylene, *P*	71.70	145.3	1.5144	64.03	162.2	1.5152	*F, L*
30.	Ethylene dibromide, *P*	...	...	....	...	...	....	
31.	Acetone, *P*	62.37	164.2	1.5162	60.19	164.0	1.5162	*D, I*
32.	Isopropyl ether, *P*	62.72	165.9	1.5172	63.25	167.0	1.5175	*A, G*
33.	Ethyl acetate, *M*	..	...	....	...	...	....	

[a] Key to letters used in table:

A. Equal in color to oil extracted with Skellysolve F.
B. Oil slightly darker than that extracted with Skellysolve F.
C. Oil darker than that extracted with Skellysolve F.
D. Oil considerably darker than that extracted with Skellysolve F.
E. Oil had pale green color.
F. Oil had slight green color, more pronounced than *E*.
G. Oil contained no solid particles before or after vacuum stripping.
H. Oil contained slight amount of suspended white solid particles before vacuum stripping.
I. Oil contained considerable amount of suspended white solid particle before vacuum stripping.
J. Oil was white solid before vacuum stripping.
K. High solvent retention, no index of refraction taken.
L. Oil considerably more viscous than that extracted with Skellysolve F.
M. A. C. S. grade or equal.
N. Commercial grade.
P. Technical grade.
R. Oil was white solid on storage at 5° C. for 24 hours, liquid at room temperature.

TABLE 5.12. RESULTS OF EXTRACTING TUNG OIL FROM PREPARED KERNELS WITH VARIOUS SOLVENTS[a].[14]

Solvent No.	Boiling Range, ° C.	Temp. Range of Bath, ° C.	Heating Period, Minutes	Pressure Range, Mm.	Iodine No., Wijs	Iodine No., Woburn	$n_D^{27.5}$		Characteristics of Oil	Value of Solvent
							Initial[b]	Final[b]		
1	26.7– 30.0	58–88	20	86–95	165.9	237.78	1.5183	1.5183	*A, H-4, L*	*U*
2	34.4– 37.8	55–80	28	72–85	165.6	238.44	1.5176	1.5177	*A, J-4, L*	*U*
3	35.0– 58.9	90–108	12	83–160	162.4	230.51	1.5168	1.5175	*A, H-2, M*	*U*
4	35.0– 60.0	71–103	18	78–120	163.6	231.84	1.5169	1.5175	*A, J-2, L*	*U*
5	54.0– 71.0	84–104	15	84–102	163.9	231.86	1.5178	1.5178	*A, H-4, L*	*S*
6	60.0– 82.2	80–96	17	80–88	161.7	225.57	1.5158	1.5173	*A, H-2, L*	*S*
7	63.8– 70.0	79–111	22	88–118	162.1	232.50	1.5170	1.5174	*A, H-4, L*	*S*
8	79.0– 82.0	77–100	14	85–90	162.4	231.84	1.5160	1.5175	*A, H-4, L*	*S*
9	79.5– 81.0	84–116	15	81–89	158.5	221.28	1.5169	1.5176	*B, F, H-2, L*	*M*
10	79.0– 83.0	90–115	26	83–120	161.4	225.90	1.5170	1.5176	*D, H-2, L*	*S*
11	87.8– 97.8	71–95	22	85–110	159.4	222.27	1.5147	1.5176	*A, H-4, L*	*S*
12	94.4–112.0	60–120	10	70–80	163.8	....	1.5170	1.5170	*B, H*	*M*
13	95.5–114.4	79–109	20	80–86	158.4	....	1.5155	1.5173	*B, H-2, L*	*M*
14	100.0–103.0	83–116	17	78–95	157.3	231.84	1.5143	1.5175	*B, H-2,* L	*S*
15	95.0–102.8	116–132	15	81–98	165.6	225.23	1.5157	1.5177	*B, H-2, L*	*S*
16	110.0–111.0	92–115	20	76–160	159.9	220.62	1.5168	1.5174	*B, F, H-2, L*	*M*
17	115.5–138.9	92–118	20	82–85	153.9	219.29	1.5136	1.5173	*B, H-2, L*	*V*
18	137.0–140.0	93–117	25	76–90	143.9	220.61	1.5159	1.5173	*D, H-2, L*	*V*
19	40.0– 41.0	50–70	15	80–100	156.6	225.23	1.5137	1.5149	*D, I, L*	*U*
20	48.4	50–70	15	80–100	161.9	224.56	1.5156	1.5157	*D, I-2, L*	*M*
20	48.4	35–120	10	80–130	163.2	226.25	1.5162	1.5162	*D, I-2, L*	*M*
21	61.0	107–145	15	77–100	161.0	224.46	1.5168	1.5175	*D, H-2, L*	*S*
22	96.8	63–98	20	84–89	157.1	....	1.5146	1.5173	*B, H-2, L*	*M*
22	96.8	105–128	9	80–130	156.8	....	1.5142	1.5142	*B, H-2, L*	*M*
22	96.8	80–110	10	80–130	164.8	....	1.5171	1.5175	*B, H-2, L*	*M*
23	76.0– 78.0	87–108	18	81–103	158.7	225.20	1.5168	1.5175	*C, H-4, L*	*M*
24	77.9	75–110	27	85–95	163.1	225.90	1.5164	1.5175	*B, J-2, L*	*M*
25	83.6	55–105	22	89–95	155.7	223.25	1.5157	1.5176	*C, H-2, L*	*M*
25	83.6	100–120	10	80–130	159.5	....	1.5165	1.5165	*C, H-2, L*	*M*
25	83.6	90–110	10	80–130	163.4	....	1.5171	1.5175	*C, H-2, L*	*M*
26	86.0– 87.5	77–91	18	73–80	149.2	211.20	1.5159	1.5177	*C, H-2, L*	*M*
26	86.0– 87.5	35–120	10	80–130	162.2	225.50	1.5162	1.5162	*C, H-2, L*	*M*
27	87.2	65–103	20	89–95	142.9	199.50	1.5139	1.5176	*C, P-4*	*M*
27	87.2	90–140	10	80–130	161.2	....	1.5155	1.5155	*C, P-4*	*M*
27	87.2	85–120	13	80–130	161.2	....	1.5169	1.5172	*C, P-4*	*M*
28	113.5	70–133	32	85–89	155.0	213.30	1.5155	1.5173	*C, G-4*	*M*
28	113.5	100–130	10	80–130	158.6	....	1.5162	1.5162	*C, G-4*	*M*
28	113.5	100–135	15	80–130	161.8	....	1.5167	1.5171	*C, G-4*	*M*
28	113.5	100–135	15	80–130	144.9	....	1.5152	1.5172	*C, G-4*	*M*
29	121.0	89–115	27	73–75	157.1	192.23	1.5169	1.5170	*C, H-4, L*	*M*
29	121.0	135–149	10	80–130	164.7	....	1.5173	1.5174	*C, H-4, L*	*M*
29	121.0	135–150	12	80–130	164.7	....	1.5172	1.5174	*C, H-4, L*	*M*
30	131.7	92–125	30	85–90	139.2	204.80	1.5180	1.5180	*E, K-4, R*	*M*
30	131.7	145–170	15	80–130	158.0	....	1.5170	1.5171	*E*	*M*
31	56.1– 56.5	77–128	18	79–115	164.2	225.90	1.5169	1.5175	*A, H-2, N*	*M*
31	56.1– 56.5	35–130	10	80–130	...	....	1.5161	1.5162	*A, H-2, N*	*M*
32	63.0– 69.0	72–95	17	87–100	161.6	223.95	1.5152	1.5175	*C, P-4*	*T, S*
32	63.0– 69.0	35–120	10	80–130	169.7	221.90	1.5154	1.5154	*C, P-4*	*T, S*
33	77.1	102–132	17	77–120	163.1	230.85	1.5158	1.5175	*A, P-2*	*S*
33	77.1	35–130	10	80–130	...	....	1.5161	1.5161	*A, P-2*	*S*

[a] Key to letters and numbers used in table:

A. Almost colorless oil.
B. Faint yellow oil.
C. Light yellow or lemon-colored oil.
D. Yellow oil.
E. Light brown oil.
F. Oil slightly cloudy.
G. Oil slightly cloudy after storage.
H. Small quantity of white precipitate after storage.
I. Faint trace of dark precipitate after storage.
J. Considerable quantity of white precipitate on storage.
K. White solid after storage.
L. Precipitate insoluble on standing at room temperature.
M. Questionable under conditions of experiment, based upon borderline quality of oil obtained.
N. Precipitate dissolved on standing at room temperature.
P. Oil entirely clear after storage.
R. Oil permanently liquid after heating short interval over Bunsen flame.
S. Oil of satisfactory quality under conditions of experiment.
T. Solvent considered unusually hazardous in storage.
U. Solvent of doubtful value for commercial tung oil extraction because of probable solvent losses due to low boiling range.
V. Solvent unsatisfactory under conditions of experiment, based upon poor quality of oil obtained.
2. After storage at approximately 5° C. for 2 months.
4. After storage at approximately 5° C. for 4 months.

[b] Differences due to evaporation of retained solvent.

TABLE 5.13. Miscibility of Solvents With Soybean Oil

M = Miscible 1:1 Solvent-to-Oil Ratio
I = Immiscible Room Temperature

SOLVENT	MISCIBILITY	SOLVENT	MISCIBILITY
Hydrocarbons			
Petroleum ether (B.P. 35–55° C)	*M*	Benzene	*M*
		Toluene	*M*
Alcohols and Phenols			
Methyl alcohol	*I*	Amyl alcohol	*M*
Ethyl alcohol	*I*	*n*-Hexyl alcohol	*M*
Ethylene glycol	*I*	Diacetone alcohol	*M*
Ethylene chlorhydrin	*I*	Cyclohexanol	*M*
Isopropyl alcohol	*I*	Furfuryl alcohol	*I*
Glycerine α monochlorhydrin	*I*	Phenol (90%)	*I*
n-Butyl alcohol	*M*	Cresol	*M*
Ethers			
Diethyl ether	*M*	Glycerol αγ diisoamyl ether	*M*
ββ′ Dichlor diethyl ether	*M*	1,4 Dioxane	*M*
Glycerol α methyl ether	*I*	Anisole	*M*
Glyceryl αγ dimethyl ether	*M*	*o*-Nitroanisole	*M*
Di-*n*-butyl ether	*M*	*o*-Anisidine	*M*
Aldehydes and Ketones			
Acetone	*M*	Benzaldehyde	*M*
Mesityl oxide	*M*	Acetophenone	*M*
Cyclohexanone	*M*	Furfural	*I*
Acids			
Acetic acid	*I*		
Esters			
Ethyl carbonate	*M*		
Halogenated Compounds			
Carbon tetrachloride	*M*	*o*-Dichloro-benzene	*M*
Chlorobenzene	*M*		
Nitrogen Containing Compounds			
Cyclohexylamine	*M*	Acetonitrile	*I*
Nitroethane	*I*	Pyridine	*M*
Nitrobenzene	*M*	Quinoline	*M*
Aniline	*M*		

TABLE 5.14. OILS AND WAXES—QUALITATIVE SOLUBILITY CHART[21]

SOLVENT	BOILING POINT	APPROX. PRICE PER GAL.	10° C.				21° C.				HIGHER TEMPERATURES[a, b]				REMARKS
			A	B	C	D	A	B	C	D	A	B	C	D	
	° C.														
Ethyl acetate	77	$1.10	100	−50	100	0	100	−50	100	0	..	100 (68)	..	100 (68)	Apparently has fairly good selective qualities; A and C appear more soluble than B. 1B and 2B separate slowly from solution
Butyl acetate	125	1.40	100	100	100	0	100	100	100	5	.			100 (50)	Has marked selectivity for oil over wax; ppt. from 1D and 2D somewhat crystalline
Amyl acetate	148	1.60	100	100	100	0	100	100	100	5	.			100 (51)	Same as for butyl acetate
Kerosene	240–500	0.12	100	100	100	0	100	100	100	5	.			100 (65)	Same as for butyl acetate
Toluene	111	0.40	100	100	100	0	100	100	100	5	.			100 (55)	Same as for butyl acetate
Xylene	142	0.40	100	100	100	0	100	100	100	5				100 (50)	Same as for butyl acetate
Turpentine	300	0.60	100	100	100	0	100	100	100	5	.			100 (51)	Same as for butyl acetate
Chlorobenzene	132	0.64	100	100	100	0	100	100	100	15	..			100 (65)	Marked selectivity for oil over wax. 1D and 2D very crystalline
Carbon tetrachloride	76	0.90	100	100	100	0	100	100	100	5	..			100 (65)	A, B, C, and D darken on standing
Tetrachloroethane	135	1.90	100	100	100	0	100	100	100	0	..			100 (50)	Good selective qualities, but A, B, C, and D darken on standing
Ethylene dichloride	...	..	..	..	..	..	..	..	..	..				..	Past experience shows this to possess good selective qualities, but that solutions darken on standing
Ethyl alcohol	78	2.70	0	0	0	0	0	0	0	0	0 (70)	0 (74)	0 (75)	0 (75)	Apparently no selective qualities
n-Propyl alcohol	97	1.00	25	15	20	0	25	15	20	0	100 (35)	100 (75)	100 (70)	100 (65)	A appears more soluble than C, and C more than B; selectivity for oil over wax

Isopropyl alcohol	83	1.00	−15	−15	−15	0	−15	−15	−15	0	100 (70)	50 (80)	100 (75)	100 (75)	Seems to have selectivity for oil over wax; oil layer increases
Butanol	117	1.40	100	30	100	0	100	30	100	0	..	100 (80)	..	100 (50)	Apparently has good selective qualities; A and C appear to be more soluble than B
Amyl alcohol	138	1.67	100	100	100	0	100	100	100	5	..	..	..	100 (55)	Apparently has marked selectivity for oil over wax
Diacetone alcohol	...	1.70	0	0	0	0	0	0	0	0	100 (77)	10 (94)	100 (88)	0 (88)	Some selective qualities at high temperatures
Acetone	56	1.00	−10	−10	−10	0	−10	−10	−10	0	0 (87)	0 (87)	0 (87)	0 (87)	Does not appear to have very good selective possibilities
Ethyl methyl ketone	81	2.00	100	−25	100	0	100	−25	100	0	..	100 (57)	..	100 (53)	Apparently has fairly good selective qualities; A and C appear more soluble than B
50% Butanol 50% Acetone	...	..	100	0	0	0	100	0	0	0	..	0 (82)	100 (82)	100 (60)	Marked selectivity for A over B, C, and D at low temperatures
Mesityl oxide	128	..	100	100	100	0	100	100	100	5	..	..	..	100 (50)	Marked selectivity for oil over wax
n-Butylaldehyde	...	..	100	100	100	0	100	100	100	5	..	..	..	100 (50)	Same remarks as for butyl acetate
Acetic anhydride	137	2.61	0	0	0	0	0	0	0	0	0 (90)	0 (90)	0 (85)	0 (50)	Has apparently no selective qualities
Glacial acetic acid	118	1.20	−15	−15	−15	0	−15	−15	−15	0	−15 (92)	−15 (92)	−15 (92)	0 (75)	Has apparently no selective qualities
Dibutyl phthalate	...	..	100	0	100	0	100	0	100	0	..	100 (85)	..	100 (60)	A and C seem more soluble than B; apparently has good selective qualities; solvent viscous
Cellosolve	...	2.03	0	0	0	0	0	0	0	0	100 (56)	100 (90)	100 (75)	100 (92)	May have some selective qualities at high temperatures
Methyl Cellosolve	124	1.95	−15	0	−10	0	−15	0	−10	0	−15 (94)	0 (92)	−10 (90)	0 (50)	Apparently no selective qualities
Butyl Cellosolve	134	2.48	100	100	100	0	100	100	100	0	..	..	..	100 (50)	Appears to have good selective qualities; marked selectivity for oil over wax

A—10 cc. Texas oil and 10 cc. solvent; B—10 cc. Pennsylvania oil and 10 cc. solvent; C—5 cc. Texas oil, 5 cc. Pennsylvania oil, and 10 cc. solvent; D—10 cc. melted wax and 10 cc. solvent.

[a] Numerical values represent the apparent percentage increase or decrease (negative values) in the solvent layer.

[b] Temperatures are indicated by numbers in parentheses and are in degrees Centigrade.

ponents of the extract phase. These specific groups include OH, NH_2, CHO, SCN, NO_2, COOR, etc.

"V. Two or more similar specific refining groups are generally inferior to one. Polyhydric phenols such as resorcinol are less effective than carbolic acid, but various means have been employed to enhance the refining action of the former. Ethylene and diethylene glycols are preferred to glycerol.

"Two dissimilar specific groups are usually superior to two which are alike. Thus, ethylene chlorohydrin or ethylene glycol monoacetate are more potent than ethylene glycol. Ortho-substituted compounds, such as guaiacol, salicylic acid, or *o*-anisidine, are superior to catechol but not to resorcinol.

"Substituted ethers and substituted esters exert much more refining action than the simple ethers and esters. Dichloroethyl ether is effective, but ethyl ether fails to refine.

"Certain substances normally crystalline, such as furoic acid or *p*-chloroaniline, are effective solvents, but only when they can be induced to separate from the rosin solution in liquid phase. The latter state sometimes is attained on liquefying with a small proportion of water or an organic solvent, also at times by dissolving in a suitable liquid such as alcohol or ethylene glycol. The selective solvency of poorly immiscible liquids such as acetic acid or acetonitrile may also be enhanced by the latter procedure.

"Inorganic reagents such as liquid sulfur dioxide, sulfur dioxide dissolved in an organic liquid such as acetone, and certain inorganic salts dissolved in organic liquids refine rosin by the selective immiscible solvent procedure."[17]

Petroleum Refining

The petroleum industry, which had long been a supplier of solvents to other industries, has in recent years turned to the use of selective solvents to improve its own products. With these selective solvents it is possible to separate the more valuable constituents from a complex mixture in as nearly a pure state as possible. Lazar Edeleanu had the distinction of being the first to use the principle of selective solvents. He treated kerosene with liquid sulfur dioxide and obtained a better-burning product. In consequence, other solvents were soon proposed as selective solvents for different petroleum fractions. Ferris[18] states that a selective solvent should be nonreactive with the oil, capable of extracting the naphthenic from the paraffinic constituents when used in reasonable amounts, and that at the same time it should be completely separable.

Hill[19] believes that, of the host of proposed solvent combinations, liquid propane, acetone, acetone benzene, and trichloroethylene are in a class by themselves. Gohre[20] contributed levulinic acid as an excellent means for separating aromatic from aliphatic substances. Poole[21] tabulated data concerning the relative solubilities of wax and oil in several organic solvents. This work was conducted with the object of encouraging the commercial use of extraction processes for the separation of oils and waxes.

The consumption of solvents in the petroleum refining industry[22] has reached imposing proportions. Millions of pounds of methyl ethyl ketone are used each year in oil dewaxing plants. High octane ethyl fluid manufacture requires hundreds of millions of pounds per year of ethylene dichloride and ethylene dibromide.

Lubricating oils, like gasoline, ordinarily receive chemical treatment or are subjected to treatment with chemical solvents. Petroleum fractions containing lubricants are variable mixtures of paraffin, naphthenic, aromatic and asphaltic hydrocarbons as well as derivatives and related materials. Separation of the hydrocarbons is performed by one means or another in order to produce a finished lubricant having a composition suited to a particular service. Treatment with sulfuric acid and contacting with clay have long been practiced and continued to be used to improve color, odor and stability. The use of solvent extraction for manufacturing preferred lubricants, and the addition of chemicals to lubricants to impart special qualities, has increased greatly in recent years. Solvents which have been used either alone or in combination include acetone, benzol, cresylic acid, sulfur dioxide, ethylene dichloride, dichloroethyl ether, furfural, nitrobenzene, phenol and propane. Losses of solvents are small and are confined to physical losses from equipment and slight solution in the oils being processed.

The principal prewar solvent requirements of the refining industry have been estimated as follows:

TABLE 5.15. Principal Prewar Solvent Requirements of the Refining Industry[23]

(Chemicals Consumed: 12-Month Consumption Ending October 1, 1941 (pounds))

Acetone	1,829,000	Formaldehyde	71,000
Alcohol, ethyl	700,000	Furfural	2,400,000
Alcohol, isopropyl	300,000	Glycerin	80,000
Carbon tetrachloride	1,240,000	Methyl ethyl ketone	1,185,000
Chloroform	126,900	Nitrobenzene	1,086,000
Cresol	3,400,000	Phenol	4,137,000
Dichloroethyl ether	404,000	Tetraethyl lead fluid	77,000,000
Diethylene glycol	247,000	Toluene	1,600,000
Ethyl acetate	600,000	Tricresyl phosphate	696,200
Ethylene dichloride	1,984,000	Turpentine	8,100,000

In his studies of selective extraction of hydrocarbons, Francis[24] determined the critical solution temperatures of a large number of different solvents. The results of his researches and his valuable conclusions are shown in Tables 5.16 to 5.19.

Anti-freeze[25]

Anti-freezes are basically of two types, the volatile and the nonvolatile. The volatile type includes methanol, ethanol, and isopropanol; the nonvolatile includes ethylene, propylene and diethylene glycols, glycerol, sugars and various inorganic solutes. Of the volatile types methanol is the most efficient because it has the lowest molecular weight, as shown in Fig. 5.8. Ethylene glycol is easily the most efficient of the nonvolatile type of anti-freezes. Consumption of anti-freeze liquids currently totals 70 million gallons, as shown below.

ESTIMATED ANNUAL CONSUMPTION OF ANTI-FREEZE MATERIALS IN U.S.A.
(Millions of gallons)

	1931-32	1934-35	1935-36	1936-37	1937-38	1938-39	1939-40	1940-41	1941-42	1945-46	1946-47[1]	1948-49[2]
MeOH	2.0	5.0	7.0	9.1	9.5	9.5	13.0	14.0	18.4		20.0	22.0
Glycol	0.6	4.0	8.2	9.0	9.0	9.0	9.0	11.0	15.75	13.0	13.5	23.0
EtOH	46.0	36.0	27.9	32.4	23.3	20.0	20.0	21.0	19.25	45.0	36.5	25.0
Glycerol	1.0	0.8	0.2									
i-PrOH		0.8	1.5		2.0	2.0			1.92			
Misc.	0.5				1.0	1.0		2.0				
Total	50.1	46.6	44.8	50.5	44.8	41.5	42.0	48.0	55.32	58.0	70.0	70.0

[1] Chem. and Eng. 25, No. 38, 2782 (Sept. 22, 1947).

[2] C.I., "Newsletter", Feb. 1948.

As summarized by the Maintenance Methods Coordinating Committee of the Society of Automotive Engineers, the essential requirements for an acceptable anti-freeze material are:

1. Ability to lower the freezing point of water to the lowest winter operating temperature likely to be encountered.
2. Incapability of imparting any undesirable properties to the water which would interfere with its primary function of efficient engine cooling.
3. Satisfactory chemical stability in service, and the ability to protect cooling system metal from corrosive action of water.

Other additional desirable characteristics are:

a. Availability at low cost.
b. Minimum effect on rubber hose connections.

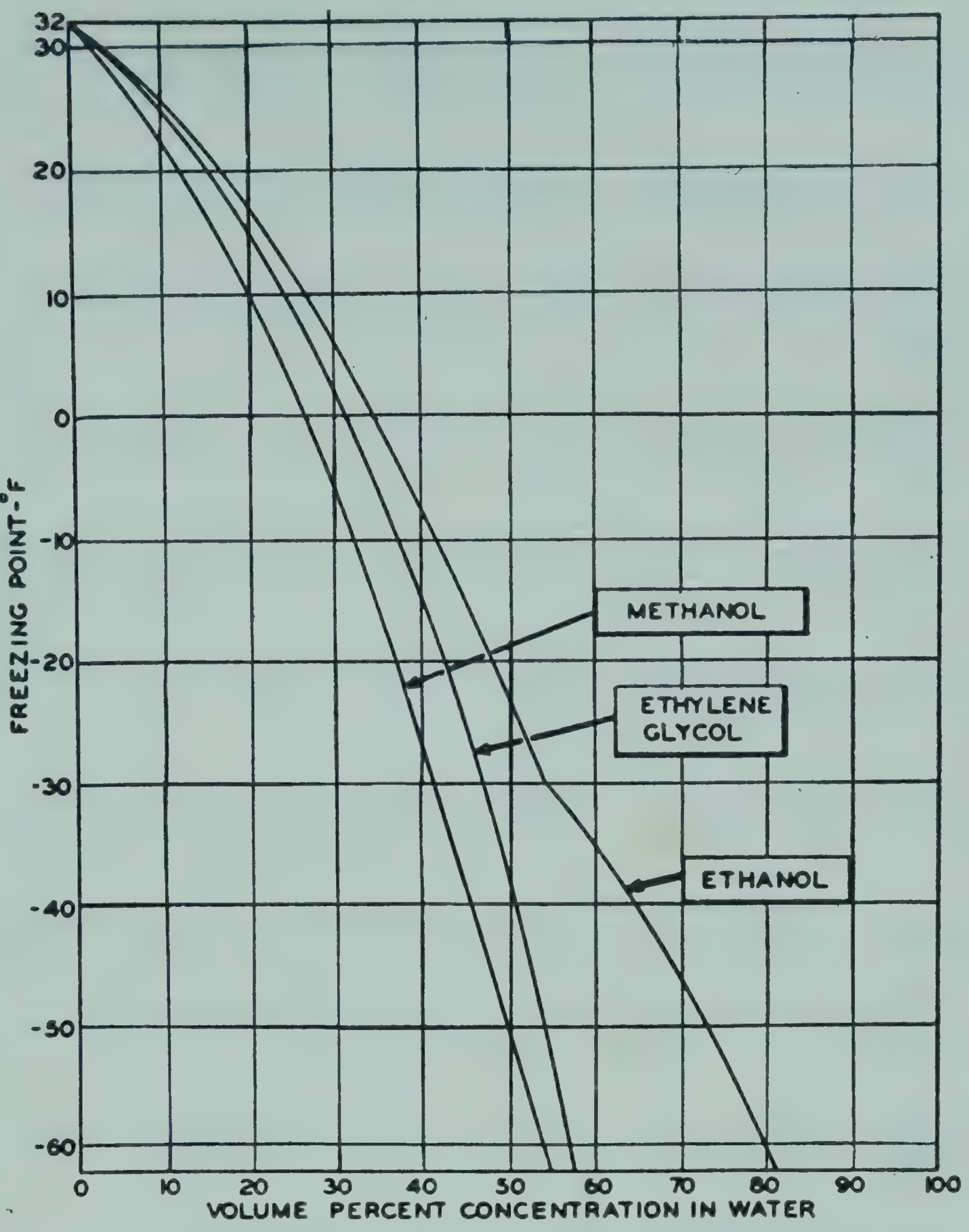

Figure 5.8. Freezing Points of Common Anti-Freeze Solutions.[26]

c. Low partial pressure.
d. Freedom from unpleasant odor.
e. Minimum effect on automobile finishes.
f. Low coefficient of expansion.

Rubber

Turpentine was the earliest commercial rubber solvent, but its use has long since given way to benzene, naphtha and other cyclic and aliphatic compounds. Twiss[27] listed the following solvents used in the modern rubber industry: carbon disulfide, carbon tetrachloride, cyclohexane, *n*-decane, "Dekalin" ethyl ether, ethylene dichloride, *n*-hexane, *n*-heptane, "Hexalin," methyl Hexalin, *n*-nonane, *n*-octane, pentachlorethane, *n*-pentane, "Tetralin," tetrachlorethane, toluene, trichlorethylene and *m*-xylene. He also classified their swelling power, which runs parallel to their solvent power, as follows: trichlorethylene, >tetrachlorethane, >pentachlorethane, >carbon tetrachloride, >chloroform, >carbon disulfide, >benzene, >toluene, >xylene, >shale naphtha, >petroleum naphtha, >kerosene,

(*Text continued on page 151*)

Table 5.16. Critical Solution Temperatures[a][24]

Solvent	*n*-Hexane	*n*-Heptane	1-Heptene	Cyclohexane	Methylcyclohexane	Iso-octane	Di-isobutene	Paraffin wax	Paraffinic Oil	Naphthenic Oil	Selectivity				
											Olefin	Naphthene	Branched chain	Oil	Mol. wt.
Acids and Anhydrides															
Acetic acid	−5*e*	10.5	...	6*e*	7	6.5	−37*e*	178	201	153	(44)	−4	+ 4	37	168
Acetic anhydride	59	68	24	52	56	66	27	160	172	143	42	10	+ 2	23	92
Propionic acid	...	<−70	...	..	...	...	...	8*e*	10	−31	..	..	..	40	>78
Chloroacetic acid	137	137	70	86	98	139	67	238	220	187	70	45	− 2	42	101
Furoic acid	166	168	...	98*e*	112*e*	184	...	267*e*	250	214	..	62	−16	45	(99)
Benzoic anhydride	79	79	...	11*e*	28*e*	91	20*e*	123	124	66	(71)	60	−12	58	44
Phthalic anhydride	197	186	129	128	132	193	126	215	209	160	62	54	(− 7)	52	29
Anthranilic acid	219*e*	204*e*	149	118*e*	132	219*e*	150	229*e*	227*e*	175	(62)	(72)	(−15)	(53)	(25)
Alcohols															
Methanol	35	51	12	45	47	43	0	187	204	188	41	−3	+ 8	8	136
Ethanol	<−78	−60	...	...	...	−70	...	112	128	108	..	..	+10	12	172
n-Propanol	...	<−78	...	...	...	...	...	65	82	48	..	..	..	26	>143
Isopropanol	...	<−78	...	...	...	...	...	68	83	60	..	..	..	16	>146
n-Butanol	...	<−78	...	...	...	...	...	25*e*	36	1	..	..	..	(30)	>103
Isobutanol	...	<−78	...	...	...	...	...	38*e*	50	28	..	..	..	(16)	>116
sec-Butanol	...	<−78	...	...	...	...	...	18*e*	31	9	..	..	..	(16)	> 96
Isoamyl alcohol	...	<−78	...	...	...	...	...	12*e*	18	−15	..	..	..	(30)	> 90
Diacetone alcohol	10	8	−32	− 6	− 5	4	−48	94	96	65	46	15	+ 4	30	86
Methyl Cellosolve	28	48	−10	25	26	46	− 2	115	119	95	53	12	+ 2	22	67
Cellosolve	−32	−12	...	−60*e*	−40	−15	...	98	106	74	..	28	+ 3	28	110
Methyl Carbitol	85	104	57	63	68	104	55	192	200	168	48	29	0	13	88
Carbitol	12	25	−25	<− 1	<−40	28	−25	125	133	109	52	>39	− 3	20	100
Ethylene chlorohydrin	101	108	74	81	89	113	72	170	171	141	38	20	− 5	30	62
Furfuryl alcohol	115	115	76	78	93	122	79	180	183	148	41	30	− 7	34	65
Tetrahydrofurfuryl alcohol	82	82	15	40	50	93	45	150	150	115	58	37	−11	35	68
Benzyl alcohol	49	60	− 8	2	14	73	15	123	119	76	63	47	−13	45	63
Phenylethanol	33	34	−14	...	−10	49	−14	99	98	47	56	44	−15	52	65
Cinnamyl alcohol	100	102	47	39	51	115	60	152	145	97	55	56	−13	52	50

Aldehydes															
Crotonaldehyde	−21	−14	...	−31*e*	−25	−14	−70	63	69	32	56	11	0	34	77
Dicroton	−22	−24	<−78	−36*e*	−41	−16	−56	35*e*	27	−8	47	16	−8	(39)	(59)
Aldol	23	36	−26	−2	1	37	−27	116*e*	122*e*	86	63	30	−1	(33)	(80)
Paraldehyde	−61*e*	−54*e*	...	...	...	−60*e*	...	34*e*	40	12	..	..	..	25	(88)
Furfural	92	95	56	69	76	101	62	159	165	122	39	21	−6	40	64
Benzaldehyde	3	3	<−50	−22*e*	−15	16	−38	49	45	14	54	22	−13	33	46
Salicyl aldehyde	31	34	−3	5	10	42	−7	80	78	39	43	25	−8	40	46
Amines															
Aniline	69	70	26	31	41	80	36	116	115	75	44	34	−10	41	46
o-Toluidine	25	25	−25	−7	−3	35	−10	72	69	34	48	30	−10	37	47
p-Toluidine	...	...	...	...	...	<35	...	63	54	...	..	..	..	..	...
Xylidines	−22	−23	...	−49*e*	−46*e*	−11	−67*e*	34*e*	29	−14	(56)	(25)	−12	(46)	(57)
Methylaniline	...	0	...	...	...	9.5	...	...	46	...	..	..	−9.5	..	(46)
α-Naphthylamine	117	113	58	57	65	130	74	145	141	87	56	54	−17	56	32
β-Naphthylamine	143	131	...	65*e*	79*e*	147	88*e*	160	155	98*e*	(59)	65	−16	(60)	29
o-Aminodiphenyl	45	43	...	...	...	60	3*e*	88	82	28*e*	(57)	..	−17	(57)	45
p-Aminodiphenyl	134	125	70	63	72	140	82	155	142	93	57	62	−15	56	30
Diphenylamine	23*e*	26*e*	...	...	...	43	...	67	64	10*e*	..	..	(−17)	56	41
Diphenylethylenediamine	109	103	52	33*e*	48	118	62	139	134	85	54	66	−15	52	36
Phenyl-α-naphthylamine	69	63	...	...	0*e*	84	17*e*	90	70	24	(67)	(63)	−21	56	27
o-Chloroaniline	14	13	...	−25*e*	−17	26.5	−27*e*	50	46	6	(54)	35	−14	42	37
p-Chloroaniline	...	80	...	...	...	86	...	...	...	...	..	..	−6	..	...
o-Nitroaniline	233	206	...	133	147	222	151	227	216	163	71	59	−16	59	21
3,4-Nitroaminotoluene	181	173	114	107	113	190	118	191	187	129	66	67	−17	60	18
o-Phenetidine	26	28	−16	−2	−1	38	−9	80	76	35	46	29	−10	43	52
p-Phenetidine	81	83	41	46	54	92	48	139	131	90	43	32	−9	45	56
Esters															
Ethyl formate	−40	−34	...	−48*e*	−36	−42	−82*e*	65	71	41	(40)	5	+8	27	99
Ethyl acetate	...	<−78	...	...	...	...	...	12*e*	10.5	−17	..	..	.	28	>90
Ethyl acetoacetate	32	43	−2	24	26	43	−2	125	130	101	45	13	0	27	82
Ethyl lactate	8	21	−25	−2	−1	19	−30	115	121	94	48	16	+2	24	94
Ethyl oxalate	15	23.5	−26	5	5	21	−30	114	120	85	50	14	+2.5	32	91
Butyl oxalate	−58*e*	−55*e*	...	...	...	−58*e*	...	23*e*	14	−22*e*	..	..	(+3)	41	78
Methyl furoate	50	57	...	34	36	61	14	114	113	78	47	19	−4	36	57
Ethyl furoate	16	20	...	−1*e*	−1*e*	20	−30*e*	85	85	49	(50)	(19)	0	36	65
n-Propyl furoate	−28	−24	...	−48*e*	−44	−20	−70*e*	53	49	12	(50)	20	−4	39	77
n-Butyl furoate	−26	−22	...	−44*e*	−50*e*	−18	−66*e*	57	58	15	(48)	(23)	−4	43	79
n-Amyl furoate	−36	−32	...	−56*e*	−70	−28	−82*e*	51	50	9	(54)	29	−4	42	83
Methyl anthranilate	47	46	−13	16	15	58	3	101	99	55	57	31	−12	45	55
Phenyl phthalate	...	135	79	41	63	145	...	190	...	...	56	72	−10	..	45
Triphenyl phosphite	...	91	...	...	27	111	...	...	...	...	..	64	−20	..	...

TABLE 5.16. CRITICAL SOLUTION TEMPERATURES—*Continued*

Solvent	*n*-Hexane	*n*-Heptane	1-Heptene	Cyclohexane	Methylcyclohexane	Isooctane	Di-isobutene	Paraffin Wax	Paraffinic Oil	Naphthenic Oil	Selectivity				
											Olefin	Naphthene	Branched chain	Oil	Mol. wt.
INORGANIC															
Ammonia	56	63	...	59	63	61	46	None	None	None	15	− 1	+ 2	..	...
Carbon dioxide	−61	−51	...	−37	−41	−61	<−78	None	None	None	(17)	−17	+10	..	...
Sulfur dioxide	10.2	19.4	−21	12.7	16	18.7	−35	95	113	86	47	0.5	0.7	18	76
KETONES															
Acetone	−39	−28	...	−29*e*	−30	−34	−67*e*	65	77	52	(33)	− 4	+ 6	19	93
Acetonylacetone	59	68	11	...	...	72	31	...	...	..	49	..	− 4	..	...
Acetophenone	3	4	...	−16*e*	−17*e*	14	−28*e*	51	47	13	(42)	20	−10	36	47
Quinone	...	108	...	...	...	116	...	162	152	117	..	..	− 8	40	54
NITRO COMPOUNDS															
Nitrobenzene	21	17.5	...	− 4	− 3	27	−25*e*	54	53	14	(52)	23	−9.5	40	37
o-Nitrotoluene	0	−1	...	−28*e*	−20	8	−46*e*	39*e*	35	− 4	(54)	24	− 9	41	(40)
o-Nitrophenol	41	43	...	25*e*	24*e*	48	− 3*e*	81	76	32	(51)	(18)	− 5	47	38
o-Nitrochlorobenzene	41	41	...	0*e*	12*e*	49	− 4*e*	78	73	28	(53)	(35)	− 8	48	37
p-Nitrobenzyl chloride	104	103	47	56	63	111	55	139	134	80	56	44	− 8	57	36
2-Nitro-4-methylphenol	18	18	...	...	...	25	−22*e*	56	54	12*e*	(47)	..	− 7	43	38
m-Dinitrobenzene	...	...	149	143	...	...	115	238	230	169	..	..	..	65	...
2,4-Dinitrochlorobenzene	199	187	127	124	132	190	128	218	206	151	61	55	(−3)	61	31
PHENOLS															
Phenol	51	53	....	...	11*e*	66	0*e*	117	112	74	(66)	(42)	−13	41	64
o-Cresol	5	9	...	−36*e*	−29*e*	21	−45*e*	82	76	28	(66)	(40)	−12	51	73
m-Cresol	12	14	<−52	−53*e*	−27	29.5	−39	94	93	43	67	53	−16	51	80
p-Cresol	11	12	...	−51*e*	−38*e*	28	−40*e*	97	98	48	(68)	56	−16	50	85
Cresylic acid	0	0	−60	−51*e*	−37	15	−45	74	74	23	60	44	−15	51	74
o-Chlorophenol	5	6	...	−44*e*	−27	18	−43*e*	58	50	6	(61)	41	−12	48	52
p-Chlorophenol	69	67	...	13	21	80	6	111	103	55	74	51	−13	52	44
2,4-Xylen-1-ol	−70	−60	...	...	...	−45	...	21*e*	27	(−30)	..	..	−15	(54)	(81)
o-Benzylphenol	65	67	3	0	10	81	14	116	108	54	66	61	−14	58	49
Eugenol	0	3	−44	−38*e*	−30	11	−42	64	63	21	50	36	− 8	43	61
o-Hydroxydiphenyl	...	28*e*	...	...	...	49	...	77	69	18	..	..	(−21)	55	(49)
m-Hydroxydiphenyl	134	121	<56	...	60	138	67	162	156	100	69	61	−17	59	41
β-Naphthol	145	130	...	...	58*e*	150	73*e*	159	152	92*e*	(77)	(72)	−20	(63)	29
MISCELLANEOUS															
Acetonitrile	...	84	...	76	78	81	...	...	...	...	..	6	+ 3	..	...
Acetanilide	None	204	134	103	123	221	145	233	232	176	73	81	−17	57	29
n-Butyramide	174	178	141	131	139	184	128	...	...	>231	47	41	− 6	..	...
Chlorex	11	15.5	−22	−11	− 7	19	−19	70	68	34	38	22	− 4	35	55
Dioxane	−13*e*	−4*e*	...	−17*e*	−14*e*	− 7*e*	...	45	45	14	..	7	..	31	49
α-Naphthonitrile	73	67	5	25	33	85	26	92	91	42	61	41	−18	50	25
β-Naphthonitrile	79	74	...	30	35	93	29	98	95	45	64	44	−19	52	24
Pyridine	−25	−21	...	−36*e*	−40	−15	−54*e*	23*e*	25	−10	(39)	15	− 6	34	(44)
Thiocarbanilide	...	...	...	...	...	...	...	179	177	153	..	..	..	25	...

[a] Selectivities in parentheses are derived from extrapolated or other less reliable observations; values marked *e* are extrapolated.

TABLE 5.17. EFFECTS OF SUBSTITUENTS IN ORGANIC SOLVENTS ON CRITICAL SOLUTION TEMPERATURES WITH HYDROCARBONS[24]

	C.S.T., ° C.
Methyl Group (or —CH_2—)	
o-Toluidine	−44
p-Toluidine	−57
Xylidines (*o*-Toluidine)[a]	−45
Methylaniline	−70
o-Cresol	−42
m-Cresol	−32
p-Cresol	−31
Cresylic acid	−47
Xylenols (*o*- & *p*-Cresols)	−69
o-Nitrotoluene	−20
2-Nitro-4-methylphenol	−22
3,4-Nitroaminotoluene	−34
Ethanol	−91
Propanols	−52
Butanols	−44
Isoamyl alcohol	−19
Phenylethanol (Benzyl alcohol)	−24
Propionic acid	(−182)
Ethyl acetate (Ethyl formate)	−57
Methyl anthranilate	−139)
Methyl furoate	(−118)
Ethyl furoate	−35
n-Propyl furoate	−40
n-Butyl furoate	(+3)
n-Amyl furoate	−11
Acetophenone (Benzaldehyde)	(+1)
Butyl oxalate (Ethyl oxalate)	$4x-20$
Cellosolve (Methyl Cellosolve)	−52
Mean	−40
Chlorine Atom	
o-Chlorophenol	−52
p-Chlorophenol	+4
o-Chloroaniline	−61
p-Chloroaniline	+8
o-Nitrochlorobenzene	+19
2,4-Dinitrochlorobenzene	−20
Ethylene chlorohydrin	+45
Chloroacetic acid	+90
Hydrogen Atoms	
Tetrahydrofurfuryl alcohol	$4x-9$
Furfuryl alcohol (Furfural)	$2x+10$

	C.S.T., ° C.
Phenyl Group	
Aniline (Ammonia)[a]	−3
Diphenylamine	−47
o-Aminodiphenyl	−29
p-Aminodiphenyl	+42
o-Hydroxydiphenyl	−35
m-Hydroxydiphenyl	+57
Phenyl-α-naphthylamine	−57
o-Benzylphenol (*o*-Cresol)	+47
Benzyl alcohol	−29
Phenylethanol	+22
C_4H_2 Group	
α-Naphthylamine (Aniline)	+33
β-Naphthylamine (Aniline)	+48
β-Naphthol (Phenol)	+63
Mean	48
Nitro Group	
o-Nitroaniline	+118
o-Nitrophenol	(−25)
m-Dinitrobenzene	+160
2,4-Dinitrochlorobenzene (*o*-Nitrochlorobenzene)	+135
3,4-Nitroaminotoluene (*p*-Toluidine)	+139
2-Nitro-4-methylphenol (*p*-Cresol)	(−18)
Mean	133
Acetyl Group	
Acetanilide	+109
Ethyl acetate	−114
Ethyl acetoacetate	+118
Acetic anhydride	+33
CHO Group	
Salicyl aldehyde	−22
Aldol (Isopropanol)	+35
Carboxyl Group	
Anthranilic acid	+116

ISOMERIC EFFECTS

Para minus Ortho	
Cresols	11
Toluidines	−12
Chloroanilines	60
Phenetidines	55
Aminodiphenyls	74
Chlorophenols	55

Meta minus Ortho	
Cresols	10
Hydroxydiphenyls	87
Beta minus Alpha	
Naphthylamines	15
Naphonitriles	5

[a] Names in parentheses are precursors.

TABLE 5.18. CRITICAL SOLUTION TEMPERATURES OF SOLVENTS WITH CYCLIC HYDROCARBONS[24]

Number	Solvent	Naphthalene	Benzene	Styrene	Anthracene	α-Methyl-naphthalene	β-Methyl naphthalene	Phenanthrene	Diphenyl	Tetralin	Toluene	Fluorene	Ethylbenzene	Dibenzyl	m-Xylene	Methylethyl-benzene
	B.P. ° C.:	218	80	145	342	245	241	340	255	207	111	298	136	286	139	162
1	Water	...	>300 (20)	...	...	...	...	...	...	...	...	...	...	...	...	...
2	Glycerol	>250	...	...	...	...	...	...	...	...	...	...	...	...	...	...
3	Formamide	>230	...	...	...	...	...	...	...	...	...	...	...	...	...	...
4	Ethylene glycol	195	180 ±	...	217	217	216	225	217	213	210 ±	220	...	...	...	...
5	Triethanolamine	151	>155	180 ±	<197	177	178	174	185	187	...	180	...	215	...	...
6	Diethanolamine	161	...	...	<195	182	182	182	183	181	...	179	...	206	...	...
7	Acetamide	148.5 (29)	142.5 (32)	...	...	169.5 (29)	...	...	167 (29)	...	...	...	...	185 (29)	200	...
8	p-Aminoacetanilide	<140	...	...	...	165	...	...	...	...	...	...	...	...	...	...
9	Glycerol monochlorohydrin	132	...	...	...	153	155	174	...	...	...	...	...	178	...	...
10	Hydroquinone	...	...	...	...	...	...	...	...	...	...	...	...	171	...	...
11	Ethanolamine	97	103	115 ±	...	134	134	139	133	139	137	145	150	168	...	...
12	Adipic acid	...	...	...	...	...	...	...	...	...	...	...	...	<147	...	...
13	Diethylene glycol	84	92	111	...	126	127	128	129	132	134	138	155	160	162	176
14	Monoacetin	78	93	...	...	124	...	130	...	...	...	...	...	140	...	...
15	Resorcinol	98	109	...	...	108	...	111	109	94	128	105	151.5 (50)	125	148.7 (7)	...
16	Propylene glycol	100	90	...	...	...	...	...	...	...	...	...	...	...	...	...
17	p-Phenylenediamine	...	...	...	...	...	...	...	...	...	...	...	...	...	<130	150
18	m-Phenylenediamine	...	69	...	...	...	...	...	...	...	...	...	...	...	...	...
19	Lactic acid	...	66	...	...	...	...	...	...	...	100	...	...	...	124	...
20	Triethylene glycol	...	22	37	...	62	61	...	65	92	90	...	115	115	120	138
21	Benzidine	...	...	...	...	...	...	...	...	...	...	...	...	...	111	127
27	Ethylene diformate	...	<−5	−8	...	25	31	...	...	42	15	...	46	...	44	66
29	Maleic anhydride	...	...	...	...	...	...	...	...	...	...	...	...	...	<15	31
35	p-Aminoethylacetanilide	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...
38	Ammonia	...	<−21	...	...	28	...	...	...	...	−5	...	...	...	15	...
39	Methyl sulfate	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...
41	m-Dinitrobenzene	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...
44	Nitromethane	...	...	...	...	...	...	...	...	−16 (33)	...	...	<−31	...	...	−25
47	Methanol	...	...	...	...	<−78	...	...	...	...	...	...	...	...	<−78	<−78
48	Furfuryl alcohol	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...
51	Acetonitrile	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...
53	Furfural	...	...	...	...	...	...	...	...	...	<−60.7 (36)	...	...	...	−55 (36)	...
55	Acetic anhydride	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...

Number	Solvent	*sec*-Butyl-benzene	Diethyl-benzene	Cymene	Methyldi-ethylbenzene	*sec*-Amyl-naphthalene	Ethyliso-propylbenzene	*sec*-Amyl-benzene	Isopropyl Tetralin	Di-isopropyl-naphthalene	Triethyl-benzene	Di-isopropyl-benzene	Methyldi-iso-propylbenzene	Di-*tert*-butyl-naphthalene	Diamyl-naphthalene	Diamyl-benzene
	B.P. ° C.:	173	181	176	203	300	195	192	261	310	216	205	217	335	360	265
5	Triethanolamine	...	...	...	...	251	...	...	264	265	...	...	...	...	...	...
6	Diethanolamine	...	...	...	...	239	...	...	248	258	...	...	...	...	...	...
8	*p*-Aminoacetanilide	>210	...	...	...	...	...	...	...	...	...	...	...	...	...	...
10	Hydroquinone	...	...	...	...	229	...	...	235	233	...	>237	...	257	...	>256
12	Adipic acid	...	...	...	...	237	...	...	...	253	...	...	...	...	...	...
13	Diethylene glycol	191	193	194	207	199	213	210	210	214	219	219	229	231	262	262
17	*p*-Phenylenediamine	169	169	170	183	...	185	...	...	181	...	193	...	...	...	...
20	Triethylene glycol	156	160	161	172	160	177	178	179	177	188	191	203	190	246	234
21	Benzidine	158	148	157	...	...	...	...	145 ±	144	185 ±	202 ±	...	...	...	...
22	*p*-Nitroaniline	139	139	139	139	<135	150	171	<140	<132	159	172	190	...	220	...
23	*p*-Aminophenol	...	...	...	...	...	...	...	...	...	...	...	...	...	220	...
24	*o*-Nitrobenzoic acid	...	...	...	...	...	...	...	<132	...	<136	149	168	<135	200 ±	250 ±
25	*m*-Aminophenol	...	...	...	...	...	...	...	...	...	...	...	...	...	195	...
26	*p*-Aminoacetophenone	...	...	...	95	...	121	125	102	98	117	147	...	...	162	196
27	Ethylene diformate	91	89	89	101	110	104	112	112	118	116	122	131	150	181	172
28	Salicyl alcohol	...	...	...	86	80	107	104	83	96	109	126	142	...	...	...
29	Maleic anhydride	87	73	73	79	90	101	123	110	91	112	130	139	...	184	191
30	*o*-Phenylenediamine	...	...	...	...	...	...	...	...	...	...	111	...	...	...	...
31	*p*-Aminobenzophenone	...	...	...	...	...	...	...	...	...	...	...	...	...	130	177
32	*m*-Nitrophenol	...	...	...	...	...	...	...	...	...	...	...	115	...	...	...
33	Acetoacetanilide	...	...	...	...	...	...	77	...	68	77	108	...	...	148	162
34	2,4-Dinitrophenol	...	...	...	...	...	...	...	...	...	...	...	...	...	117	151
35	*p*-Aminoethylacetanilide	...	...	...	...	<50	...	82	70 ±	60 ±	84	100	113	...	135	154
36	Catechol	...	...	...	...	...	...	...	...	...	...	...	100	<100	136	144
37	Antipyrine	...	...	...	...	...	...	...	...	...	...	...	...	...	100	128
38	Ammonia	...	...	25 (*53*)	...	...	...	...	...	...	...	...	...	...	...	...
39	Methyl sulfate	−22	−13	−17	13	5	7	28	57	19	41	32	49	...	111	114
40	Phenylethanolamine	<−10	...	...	5	...	27	23	10	21	34	55	69	...	98	113
41	*m*-Dinitrobenzene	...	...	...	...	...	...	...	...	...	...	<63	...	...	<78	119
42	Sebacic acid	...	...	...	...	...	...	...	...	...	...	<120	...	...	...	...
43	2,4-Dinitrochlorobenzene	...	...	...	...	...	...	...	...	...	...	<25	...	...	51	101
44	Nitromethane (cf. *33*)	0	−4	−8	11	27	9	25	34	35	26	22	34	...	95	85
45	*m*-Nitroacetophenone	...	...	...	...	...	...	...	...	...	...	...	...	...	56	93
46	Benzyl *p*-hydroxybenzoate	...	...	...	...	...	...	...	...	...	...	...	...	...	<80	99
47	Methanol	...	−18	−33	10	49	−5	−6	57	58	19	9	32	...	...	76
48	Furfuryl alcohol	−22	−16	−19	2	0	2	11	32	18	16	20	32	...	88	82
49	Chloroacetic acid	...	...	...	...	<33	...	...	...	<38	...	...	...	...	108	56
50	Phenylhydrazine	...	...	...	...	<0	...	...	<0	7	13	27	40	...	79	81
51	Acetonitrile	−50 ±	−60 ±	−60 ±	−23	4	−30	−5	14	12	−7	−15	2	...	84	67
52	Ethylene chlorohydrin	...	...	...	−50 ±	<−78	−60 ±	−22	−27	−28	−15	−5	13	...	68	70
53	Furfural	...	...	...	...	...	...	...	...	...	...	...	−18	...	23	47
54	Phenyl phthalate	...	...	...	...	...	...	...	...	...	...	<40	<34	...	...	49
55	Acetic anhydride	<−78	−50	−50 ±	−27	−39	−35	−25	3	−13	−12	−23	−6	...	44	44

TABLE 5.19. EFFECTS OF SUBSTITUENTS IN ORGANIC SOLVENTS ON C.S.T. WITH HYDROCARBONS[24]

Solvent	Intermediates[a]	Precursor	Increment, ° C.
	Hydroxyl Group (Aliphatic)		
Ethylene glycol	13	Ethanol	374
Diethylene glycol	27, 47	Cellosolve	274
Triethylene glycol	27, 47	Carbitol	201
Glycerol	13	Propylene glycol	> 168
Propylene glycol	27, 47	Propanols	313
Lactic acid	27, 47	Propionic acid	368
Salicyl alcohol	50	*o*-Cresol	198
	Hydroxyl Group (Aromatic)		
Catechol	59	Phenol	123
Resorcinol	36, 59	Phenol	212
Hydroquinone	36, 59	Phenol	257
m-Aminophenol	...	Aniline	183
p-Aminophenol	...	Aniline	208
o-Nitrophenol (*12*)	...	Nitrobenzene	23
m-Nitrophenol	50	Nitrobenzene	152
2,4-Dinitrophenol	...	*m*-Dinitrobenzene	35
Salicyl aldehyde (*12*)	...	Benzaldehyde	30
Salicyl alcohol	36, 59	Benzyl alcohol	166
	Amino Group		
Ethanolamine	27, 47	Ethanol	290
m-Aminophenol	59	Phenol	192
p-Aminophenol	59	Phenol	217
p-Aminoacetophenone	45	Acetophenone	231
p-Aminoacetanilide	21, 35, 36	Acetanilide	231
Benzidine	26, 45	*p*-Aminodiphenyl	195
3,4-Nitroaminotoluene (*12*)	...	*o*-Nitrotoluene[b]	156
o-Nitroaniline (*12*)	...	Nitrobenzene	172
p-Nitroaniline	59	Nitrobenzene	261
o-Phenylenediamine	50	Aniline	134
p-Phenylenediamine	50	Aniline	220
Phenylhydrazine	...	Aniline	50
	Hydroxyl Group *vs.* Amino Group		
Ethylene glycol	...	Ethanolamine	82
Ethanolamine	27, 52	Ethylenediamine (*9*)	328
Diethylene glycol	...	Diethanolamine	−52
Triethylene glycol	...	Triethanolamine	−107
Formic acid (Table I)	7	Formamide	< −150
Acetic acid (*12*)	27, 52	Acetamide	−322
Hydroquinone	22	*p*-Aminophenol	97
p-Aminophenol	22	*p*-Phenylenediamine	−34
Catechol	...	*o*-Phenylenediamine	2× −12
Resorcinol	...	*m*-Phenylenediamine	2× 20
Six monophenols (*12*)	...	Corresponding anilines	−11 ±5
	Carboxyl Group		
Lactic acid	27, 47	Ethanol	265
o-Nitrobenzoic acid	59	Nitrobenzene	266
	Nitro Group		
m-Dinitrobenzene	...	Nitrobenzene	147
2,4-Dinitrochlorobenzene	59	*o*-Nitrochlorobenzene	99
2,4-Dinitrophenyl	45	*o*-Nitrophenyl	146
m-Nitroacetophenone	...	Acetophenone	127
p-Nitroaniline	...	Aniline	208
m-Nitrophenol	50	Phenol	150
	Acetyl Group		
Acetoacetanilide	50	Acetanilide	31
p-Aminoacetanilide	...	*p*-Phenylenediamine	> 80
p-Aminoacetophenone	...	Aniline	167
Ethylene diacetate	27	Ethylene glycol	2× −168
Monoacetin	...	Glycerol	< −172
m-Nitroacetophenone	...	Nitrobenzene	113
	Methyl or -CH₂- Group		
Acetamide	...	Formamide	< −81
Ethylene diacetate	...	Ethylene diformate	2× −75
Ethylphenylethanolamine	...	Phenylethanolamine	2× −43
Methyl Carbitol (*12*)	39	Diethylene glycol	−237
Methyl Cellosolve (*12*)	13, 39	Ethylene glycol	−366
Sebacic acid	29	Adipic acid	4× −61
	Phenyl Group		
Phenylethanolamine	20	Ethanolamine	−210
	Chlorine Atom		
2,4-Dinitrochlorobenzene	...	*m*-Dinitrobenzene	−23
	Isomeric Effects		
Para-ortho			
p-Phenylenediamine	...	*o*-Phenylenediamine	82
Hydroquinone	...	Catechol	134
p-Nitroaniline	50	*o*-Nitroaniline	83
Para-meta			
p-Aminophenol	...	*m*-Aminophenol	25
Hydroquinone	...	Resorcinol	45
Meta-ortho			
m-Nitrophenol	50	*o*-Nitrophenol	124

[a] Numbers refer to solvents in Table II.

[b] Comparison should be made with the meta isomer, but the two probably differ only slightly in C.S.T.

>ethyl ether. The most widely used solvents are the petroleum hydrocarbons comprising those fractions which range from n-pentane to n-decane. For reclaiming vulcanized inner tubes such depolymerizing agents as pine tar, fuel oil and "Solvenol" are used. Kerosene and turpentine will also serve as devulcanizing agents.

Sarback and Garvey[28] have studied the solubilities of the important unvulcanized rubbers, both natural and synthetic, in a wide variety of organic solvents. Their findings are given in Table 5.20.

Hydraulic Brake Fluids

Fulton[29] described the early commercial brake fluids as essentially mixtures of castor oil with a diluent, generally alcohol, diacetone alcohol or ethylene glycol ethyl ether. According to Fain[30], brake fluids now represent a market for 3 to 4 million gallons per year of lubricant oils and diluents. In addition to miscibility with castor oil, suitable diluents must not be injurious to rubber, thereby effectively eliminating chlorinated hydrocarbons and ketones. Some of the more important alcohols, glycols and glycol ethers utilized in commercial castor oil-base fluids have been studied by Shough[31] and are shown in Table 5.21 (page 158).

Textile Industry

A mixture of soap and an organic solvent has the property of quickly loosening dirt, oil, fats, greases and waxes from fabric and, at the same time, of dissolving or suspending these substances in the soap-solvent-water mixture. Many of these mixtures have the added properties of wetting and penetration and are, therefore, used in the textile industry.

Solvents such as amyl alcohol, phenols, hydrogenated phenols and naphthalenes, pine oil, red oil, high aliphatic acid and their sulfonated products, xylene, triethanolamine and so forth, are used in oil-solvent, soap-solvent, and oil-soap-solvent mixtures in textile processing. Some of these processes comprise bleaching, lubricating, wetting-out, scouring and dyeing, keir-boiling, starching, degreasing, mercerizing and finishing. In many of these processes the solvent not only reduces the time of operation but aids in penetration and dispersion.

Freedland[32] regards petroleum ether as the best solvent for degreasing wool because of its comparative cheapness. With modern means of equipment, it is quite safe to handle. Solvent naphtha is used considerably as a solvent for fats and oils, while benzene, on the other hand, is used in the extraction of cotton waxes. Hydrogenated coal-tar solvents, phenols, naphthalenes, and ketones and their sulfonated derivatives are solvents for oils, fats and waxes. These solvents, when they are mixed with soluble oils and soaps, are used as detergents. Benzine soaps dissolved in amyl alcohol, ether, chloroform, carbon tetrachloride and benzine are good fat solvents and are extensively used in the cleaning industry.

(Text continued on page 158)

TABLE 5.20. Solubilities of Unvulcanized Rubbers[28]

	Boiling point °C 760 mm.	Natural pale crepe	German Buna-S	GR-S	Hycar OS-10	Butadiene methylmethacrylate copolymer	GR-I (butyl)	GR-M (neoprene)	Perbunan #26	Hycar OR-15	GR-P ("Thiokol")	Plasticized polyvinyl chloride
I. Hydrocarbons												
A. Aliphatic	69	FD	FD	FD	MG	MD	FD	ML	SL	N	N	N
Hexane												
Hi-Test gasoline	38–141	FD	FD	FD	FL	FD	FD	ML	SL	N	N	N
Kerosene	165–257	FD	SD	SD	FL	FD	SD	SL	N	N	N	N
Mineral oil-aniline pt. 104° C	—	FG	MG	MG	ML	MG	MG	SL	ML	N	N	N
B. Alicyclic												
Cyclohexane	80.8	FD	FD	FD	MD	FD	FD	MD	SL	N	N	N
C. Terpene												
Pinene	156	MD	MD	MD	FG	FD	MD	MD	FL	FL	N	SL
Dipentene	175–190	FD	FD	FD	MD	FD	FD	FD	FL	N	ML	SL
Turpentine	160–180	FD	FD	FD	MD	FD	FD	FD	FL	N	ML	SL
D. Aromatic												
Benzene	80.4	FD	FD	FD	FD	FD	FD	FD	FD	FL	FD	N
Toluene	111	FD	FD	FD	MD	FD	FD	FD	FD	FL	FL	N
Xylene	138–142	FD	FD	FD	FD	FD	FD	FD	FD	FL	FL	N
p-Cymene	175–176	FD	FD	MD	MD	FD	MD	FD	MD	FL	ML	N
Ethyl benzene	135.7	FD	FD	MD	MD	FD	MD	FD	FD	FL	FL	N
Styrene	145–146	FD	FD	FD	FD	FD	FD	FD	FD	FD	FD	FL
Tetrahydronaphthalene (Tetralin)	205	FD	FD	SD	SD	FD	MD	FD	MD	MG	FD	N
Amyl naphthalene	279–310	MD	SD	SD	SD	MD	MD	FD	MG	SG	FL	

II. HALOGENATED HYDROCARBONS												
A. Aliphatic												
Chloroform	61.2	FD	FD	FD	FD	FD	MD	FD	FD	FD	FD	ML
Carbon tetrachloride	76.7	FD	FD	FD	FD	FD	FD	FD	FL	N	N	N
Ethylene dichloride	83.5	FD	FD	FD	FD	FD	FG	FD	FD	FD	FD	SD
Isopropyl chloride	35	FD	FD	FD	FD	FD	FD	FD	FD	FG	ML	FL
Dichloro difluoro methane (Freone #12)	−28	FG	SL	SL	SL	SL	SG	N	N	N	N	N
Dichloro fluoro methane (Freone #21)	8.9	FD	SD	SD	MD	SD	MD	FG	FD	MD	MD	FL
B. Aromatic												
Chlorobenzene	132	FD	FD	FD	FD	FD	MD	FD	FD	FD	MD	ML
Fluorobenzene	84	FD	FD	FD	FD	FD	MD	FD	FD	FD	MD	FL
Chlorotoluene	159–162	FD	FD	FD	MD	FD	MD	FD	FD	FD	SD	ML
Ethyl pentachlorobenzene	—	SD	MD	MD	MD	MD	SD	MD	FL	ML	N	N
o-Chloronaphthalene	263	MD	FG	FG	FG	MD	MG	FD	MD	MD	MD	
Halowax oil	—	MD	MD	MD	SD	MD	MG	MD	MD	MD	N	N
Amyl chloronaphthalene	—	SD	FG	FG	SG	MD	MG	MD	FG	N	ML	N
III. HYDROXY COMPOUNDS												
A. Alcohols												
Ethyl alcohol	78.3	N	N	SL	N	N	N	N	N	N	N	N
Isopropyl alcohol	82.4	ML	FL	FL	ML	ML	N	ML	FL	ML	ML	N
Amyl alcohol	137.8	N	N	N	N	N	N	N	ML	N	N	N
Benzyl alcohol	204.7	N	N	ML	ML	FL	N	FL	MD	MD	FD	N
Ethylene glycol	197.2	N	N	N	N	N	N	N	N	N	N	N
Diethylene glycol	244.8	N	N	N	N	N	N	N	N	N	N	N
Glycerin	290	N	N	N	N	N	N	N	N	N	N	ML
Terpineol	218–221	MG	MG	MG	ML	FG	SL	N	FL	N	N	N
B. Phenols												
Phenol	183	FL	N	SD	MD	MD	N	FL	MD	MG	FD	N
Cresol	190–203	N	N	FL	MG	MD	N	SG	MD	SD	MD	N
p-Tertiary butyl catechol	285	FL	N	N	FG	MD	N	N	FG	MG	FG	N

TABLE 5.20. *Continued*

	BOILING POINT °C 760 MM	NATURAL PALE CREPE	GERMAN BUNA-S	GR-S	HYCAR OS-10	BUTADIENE METHYLMETHACRYLATE COPOLYMER	GR-I (BUTYL)	GR-M (NEOPRENE)	PERBUNAN #26	HYCAR OR-15	GR-P ("THIOKOL")	PLASTICIZED POLYVINYL CHLORIDE
IV. CARBOXY ACIDS												
Glacial acetic acid	118.1	N	N	FL	FL	N	FL	N	N	N	N	N
Lactic acid	119 (12 mm)	N	N	N	N	N	N	N	N	N	N	N
V. ETHERS												
Diethyl ether	34.5	FD	FD	MD	MD	FD	FG	FL	N	N	N	N
Isopropyl ether	68.4	FD	FD	FD	SD	FD	FG	FL	N	N	N	N
Phenyl ethyl ether	172	MD	MD	MD	SD	FD	MG	SD	FD	SD	FL	N
Dibenzyl ether	295–298	MD	MD	MD	MD	FD	N	MD	MD	MD	SD	SL
Dioxane	101.1	SD	SD	SD	MD	FD	N	FD	MD	MD	FD	FL
Dioxolane	74	FL	SD	FD	FL	FD	FL	SD	MD	MD	MD	FL
VI. AMINES												
Ethylene diamine	117.2	N	N	FL	ML	N	N	N	N	N	SD	N
Dicyclohexylamine	115–116 (8 mm)	FG	FG	FL	SD	SD	FG	FG	FL	N	ML	N
Diethylamine	55–56	N	N	N	N	N	N	N	FG	N	N	N
Aniline	184.4	N	N	SL	MG	FL	ML	FL	MD	MD	MD	N
Dimethylaniline	194	FD	FD	FD	FD	FD	MG	FD	FD	FD	FD	MD
Phenylhydrazine	243.5	N	N	FL	MG	FG	ML	FG	FG	MG	FD	N

VII. Nitro Compounds												
A. Aliphatic												
Nitromethane	101.2	N	N	N	FL	SD	N	FL	FD	FD	N	N
Nitroethane	114.0	N	SL	SL	FL	FD	N	FL	FD	MD	N	ML
1-Nitropropane	131.6	SL	SL	FL	FL	MD	N	FL	MD	MD	N	FL
1-Chloro-1-nitro ethane	122–128	MD	FD	FD	FD	FD	MD	FD	FD	FD	SD	ML
B. Aromatic												
Nitrobenzene	210	MG	SD	MG	MD	FD	N	FD	MD	MD	MD	MD
VIII. Aldehydes												
Furfural	161	N	N	N	N	N	N	N	FD	FD	FL	N
Benzaldehyde	179.5	FL	SD	MD	MD	FD	N	FD	FD	FD	FD	FL
n-Hexaldehyde	128.6	MG	MG	MG	MG	SD	N	N	FD	FD	N	N
IX. Ketones												
Acetone	56.1	N	N	N	SL	FL	N	FL	FD	FD	N	FL
Methyl ethyl ketone	80.6	FL	ML	MG	SD	FD	SL	FD	FD	FD	N	SD
Diisopropyl ketone	123.7	FL	ML	MG	SD	FD	SL	FD	FD	FD	N	SD
Acetophenone	202	FL	FG	SD	SD	FD	N	FD	FD	MD	FD	SD
Cyclohexanone	155–157	SD	SD	MD	SD	FD	SL	FD	FD	MD	FD	SD
Phorone	197.9	SD	SD	SD	FG	FD	N	MD	MD	MD	FG	FL
Mesityl oxide	128	FD	FD	FD	FL	FD	FL	FD	FD	MD	N	SD
X. Esters												
Methyl formate	32.3	FL	FL	FL	FL	FG	SL	N	SD	SD	ML	N
Ethyl acetate	77.1	FL	N	FL	FL	FG	ML	MD	MD	MD	N	ML
Butyl acetate	126.3	FD	FD	FD	MD	FD	ML	FD	MD	MD	N	ML
Butyl stearate	220–225 (25 mm)	MD	SD	SD	FL	MD	MG	MD	N	N	N	N
Isopropyl acetate	88.4	FL	FG	FG	SD	FD	N	FD	FD	SD	N	FL
Ethyl oxalate	186.1	N	N	N	SL	N	N	FL	FG	MD	N	N
Amyl borate	143–147 (10 mm)	FD	SD	SD	MG	N	FG	N	N	N	N	N

TABLE 5.20. *Continued*

	BOILING POINT °C 760 MM	NATURAL PALE CREPE	GERMAN BUNA-S	GR-S	HYCAR OS-10	BUTADIENE METHYLMETHACRYLATE COPOLYMER	GR-I (BUTYL)	GR-M (NEOPRENE)	PERBUNAN #26	HYCAR OR-15	GR-P ("THIOKOL")	PLASTICIZED POLYVINYL CHLORIDE
Benzyl benzoate	323–324	FL	SD	SD	MG	FG	N	MD	FG	MD	MD	N
Ethyl silicate	168.1	SL	ML	N	N	ML	N	N	N	N	ML	N
Ethyl acetoacetate	180.7	N	N	N	N	N	N	ML	MD	FD	N	N
Triacetin	258–259	N	N	N	N	N	N	N	N	N	N	N
Dibutyl phthalate	339.2	SL	MG	MG	MG	FG	N	MD	MG	SD	N	FL
Dioctyl phthalate	216 (5 mm)	MG	MG	MG	SD	SD	N	SD	SG	N	N	FL
Tricresyl phosphate	295 (13 mm)	N	ML	ML	ML	FL	N	ML	MG	MG	N	FL
Tributoxy ethyl phosphate	—	SL	SL	ML	ML	FL	ML	FL	FG	MD	N	ML
Butyl acetyl ricinoleate	220–235 (4 mm)	FL	MD	MD	MD	FL	N	MD	MD	N	MD	FL
Methyl methacrylate	—	FD	FD	FD	SD	FD	ML	FD	FD	MD	SL	FL
Cottonseed oil	—	MG	MG	MG	MG	MG	N	N	SL	N	N	N
XI. Mixed Compounds												
A. Hydroxy Amines												
Triethanolamine	208 (10 mm)	N	N	ML	ML	N	N	ML	N	N	ML	N
B. Alcohol Ethers												
"Cellosolve"	135.1	FL	FL	N	N	FG	N	N	FL	N	N	N
Butyl "Cellosolve"	171.2	N	N	N	N	FL	N	ML	N	N	N	N
"Cellosolve" acetate	156.3	ML	ML	FL	ML	FL	N	MD	MD	MD	N	N
"Carbitol"	201.9	FL	N	ML	ML	FL	N	N	N	N	N	N
C. Chlorinated Alcohols												
Ethylene chlorohydrin	128.7	FL	N	ML	ML	N	N	N	MD	MD	FL	N

XII. HETEROCYCLICS												
Piperidine	106	FD	FD	MD	SD	FG	MD	FD	FG	MG	FD	SD
Furan	31.5	FD	FD	FD	FG	FD	FL	FD	FD	FG	N	N
Thiophene	84	FD	FD	FD	FD	FD	FL	FD	FD	FD	FD	FL
Pyridine	115	FG	FD	MD	FD	FD	N	FD	FD	FD	MD	SD
Pyrrole	130	FL	N	N	N	N	N	FD	FD	FD	FD	N
XIII. SULFUR COMPOUNDS												
Carbon disulfide	46.2	FD	FD	FD	FD	FD	MD	FD	SD	ML	FG	N
Ethyl mercaptan	36–37	FD	FD	FD	FG	FD	FD	FD	FD	FG	FG	N
Liquid sulfur dioxide	−10	ML	ML	ML	ML	ML	N	SL	MD	FD	FD	ML
XIV. MISCELLANEOUS												
Acrylonitrile	78–79	N	N	MD	MD	FL	FL	SL	MD	FD	N	N
Formamide	193d	N	N	N	N	N	N	N	N	N	N	N
"Dispersing Oil #10"	225–300	FD	MD	MD	MD	FD	FL	MD	MD	MD	MG	FL
"Bardol B"	230–300	FD	MD	MD	MD	FD	MG	FD	MD	MD	MG	FL
"Nevoll"	—	MG	MG	FG	SD	FG	N	FL	FL	FL	N	FL
Liquid ammonia	−33.4	SL	SL	SL	SL	SL	SL	N	N	ML	FG	ML
"Circo Light Processing Oil"	—	SD	FL	FL	ML	FL	FL	FL	N	N	N	N

KEY
Rate of Action
S—Slow
M—Moderate
Fast

Type of Action
L—Limited Swelling and/or softening
G—Gelling or unlimited swelling
D—Dissolving
N—No apparent effect

TABLE 5.21. Materials Used in Blends

Raw castor oil
Bodied castor oil
"Cellosolve"
Butyl "Cellosolve"
"Carbitol"
Butyl "Carbitol"
"Carbitol acetate"
Dibutyl phthalate
Isoamyl alcohol
tert-Amyl alcohol
2-Ethyl butyl alcohol
Methyl isobutyl alcohol
sec-Heptyl alcohol
n-Hexanol
n-Octyl alcohol
Tetradecanol
Diacetone alcohol
Ethylene glycol
Propylene glycol
Mixture C_5–C_8 alcohols
Mixture C_7 alcohols

Dry Cleaning

The sartorial cleanliness of modern civilization is continually demanding new and better solvents for dry cleaning. In cleaning dyed garments all dirt, discoloration and stains must be removed, but the dye must not be affected. An ideal dry-cleaning solvent should have the following attributes: it should not affect the garment or the dye; it should be chemically inert, stable, odorless, nontoxic and immiscible with water; its distillation range should be close; it should be volatile but not too volatile; and it should have a high flashpoint or be nonflammable. A warm solution of soap is one of the best cleaning agents, but its short-comings of removing dye and shrinking or felting fabric restrict its use. Benzine, benzene, and solvent naphtha have been used in dry cleaning but are dangerously flammable. Further, benzine is toxic; it affects women more readily than men, producing headaches, giddiness, vomiting and a state of incipient narcosis. Benzene, like benzine, is highly volatile and is still more toxic. White spirits is a heavier fraction than benzine and is less of a fire hazard. Solvent naphtha is related to benzene in the same manner that white spirits is to benzine. The halogenated nonflammable hydrocarbons are more widely used in Europe than in America.

According to Brown[33] carbon tetrachloride approaches the ideal dry-cleaning solvent more nearly than does any other commercially known liquid. It is an excellent solvent for grease, oil, fats, resins and stains, with the added virtues that it has a pleasant odor and does not affect fiber garments. Trichloroethylene and perchloroethylene are now included among the better dry-cleaning solvents. One of the most widely used petroleum products in the dry-cleaning industry is white spirits, known as Stoddard Solvent. The following are the required specifications of the U. S. Bureau of Standards:

STODDARD SOLVENT

(Dry Cleaning)

Material: A petroleum distillate conforming to the requirements given herein.
Appearance: Clear and free from suspended matter and undissolved water.
Color: Water-white or not darker than 21 by Saybolt chromometer.
Odor: Sweet.
Flash point: Not lower than 100° F. ("Tag" closed tester).
Corrosion test: A clean copper strip shall show not more than extremely slight discoloration when submerged in the solvent for 3 hours at 212°F.
Distillation range: Not less than 50 per cent shall be recovered in the receiver when the thermometer reads 350°F. The dry or end point shall be not higher than 410°F. No tolerance shall be allowed above 410°F.
Acidity: The residue remaining in the flask after the distillation is completed shall not show an acid reaction.
Doctor test: Negative.
Sulfuric acid absorption test: Not more than 5 per cent of the solvent shall be absorbed by concentrated C. P. sulfuric acid (specific gravity, 1.835) (approximately 93.2 per cent).

Insecticides

Considerable quantities of hydrocarbon diluents, ketones, alkanolamines, and other solvents are being consumed in the preparation of concentrated solutions of the synthetic insecticides and herbicides, such as DDT, hexachlorobenzene and 2,4-D.[34] Useful solvents for these materials are shown in Tables 5.22 to 5.24. Gnadinger and Corl evaluated numerous solvents for the extraction of pyrethrum and found ethylene dichloride to be the most suitable.

The heat of mixing data shown in Table 27 (p. 175) were obtained by mixing acceptor and donor liquids.[38]

Zein

According to Manley and Evans,[39] solvents for zein can be divided into two groups: the primary solvents which are capable of dispersing zein, and the secondary solvents which enhance the solvent power of the first group. Some of the primary solvents contain acid, amide, amine, or hydroxyl groups; however, this does not mean that all compounds containing these groups are solvents for zein. Compounds which are electron acceptors in forming hydrogen bridges are secondary solvents for zein; examples of these are acetoacetic ester, formaldehyde, chloroform, and nitromethane. These workers have thoroughly investigated a number of binary and ternary solvent systems for zein and have pictured their results in a number of diagrams (Figs. 5.9, 5.10, page 168–171).

(Text continued on page 172)

TABLE 5.22. PHYSICAL PROPERTIES[1] OF SOME USEFUL SOLVENTS FOR DDT

MATERIAL	DENSITY LB. PER GAL.	BOILING POINT OR RANGE °C	FLASH POINT °F	SOLUBILITY OF DDT LB. PER GAL. OF SOLVENT
Chlorobenzene	9.2	132	88	6.2
Cyclohexanone	7.9	157	122	9.7
o-Dichlorobenzene	10.9	180	167	5.0
Isophorone	7.7	215	205	6.2
Mesityl oxide	7.1	128	90	5.4
Methyl isobutyl ketone	6.7	116	75	3.9
2-Nitropropane	8.3	120	103[2]	3.3
Tetrahydronaphthalene	8.1	207	180	5.1
Trichloroethylene	12.2	88	—	5.3
Amsco-solv F	7.3	177–213	135	2.8
Solvesso No. 1	6.7	93–135	<80	3.9
Solvesso No. 2	7.1	—	80	3.8
Solvesso No. 3	7.3	173–210	155	2.8
S/V Culicide Oil B or PD-428-G	8.6	195–over 350	280	4.0
PD-544-A	8.6	304–404	335	3.3
PD-544-B,	8.2	262–338	270	3.8
PD-544-C, regular	7.4	200–277	190	2.8
PD-544-C, special, new fraction	7.7	200–277	175[3]	3.7
PD-544-B, treated	8.2	—	280	3.4
Sovasol 74	7.0	136–182	87[3]	3.5
APS 202	8.5	288–377	260	3.8
Velsicol AR-40, July 1944	7.8	—	157	4.0
Velsicol AR-40, monomethyl, cut	8.1	220–243	215	4.9
Velsicol AR-50	8.1	236–269	230	4.6
Velsicol AR-60	8.2	240–290	245	4.8
Velsicol NR-70	8.7	258–357	300	4.3
Xylene, 10-degree	7.2	135–145	80	4.4
Solvent naphtha (industrial xylene)	7.2	130–155	90	4.3
Hi-Flash solvent	7.3	150–200	114	4.0
Crude light solvent	7.3	135–180	80	4.8
Cumene fraction	7.3	165.5–175.5	131	3.5
Heavy solvent	7.8	160–270	136	4.8
Pale yellow Hi-Flash solvent	7.2	155–200	—	3.3
K-327	8.4	230–270	236	5.6
Neutral oil	8.4	—	184	5.6
Kolineum	9.1	—	240	4.8
Special hydrocarbon oil	8.4	—	170	4.4
Hydrocarbon oil	8.3	190–300	217	5.8
Laksol	7.2	87–169.5	<80	5.2

---

[1] All boiling ranges and some values for density and flash point are approximate and were taken from the literature. All flash points are in Cleveland open cup, unless otherwise noted.

[2] Tagliabue open cup.

[3] Tagliabue closed cup.

TABLE 5.23. SOLUBILITY OF DDT IN VARIOUS SOLVENTS AT 27° TO 30°C.[35]

MATERIAL	DETERMINED BY—		SOLUBILITY OF DDT	
	Synthetic method	Refractive index method	Per 100 ml. of solvent	Per 100 grams of solvent
	Individual Substances			
			grams	grams
Acetone	x	—	58	74
Acetonyl acetone	x	x	38	39
Acetophenone	x	x	67	65
Amyl acetate	x	x	39	44
alpha-*n*-Amyl cinnamaldehyde	x	—	27	28
Anisole	x	x	70	70
Benzene	x	—	78	89
Benzyl acetate	x	x	45	43
Benzyl alcohol	x	x	12	11
Benzyl benzoate	x	x	42	38
Benzyl ether	x	x	41	39
Bicyclohexyl	x	—	9	10
Butyl lactate	—	x	21	21
Butyl *dl*-malate	—	x	17	16
Butyl mesityl oxide oxalate (Indalone)	x	x	38	35
Butyl stearate	x	x	8	9
Carbon tetrachloride	x	x	45	28
p-Chloroacetophenone	x	x	39	33
Chlorobenzene	x	x	74	67
2-(2-Chloroethoxy) ethyl-2,4,5,6-tetrachlorophenyl ether	x	—	24	16
alpha-Chloronaphthalene	x	x	55	46
Cinnamaldehyde	x	x	25	22
Cumene	x	x	37	43
Cyclohexane	—	x	15	19
Cyclohexanol	x	x	10	11
Cyclohexanone	x	x	116	122
Cyclohexyl benzoate	x	x	46	44
2-Cyclohexylcyclohexanol	x	—	<1	—
Cyclohexyl lactate	—	x	31	29
Cyclopentane carboxylic acid, methyl ester	x	x	30	32
p-Cymene	x	x	29	34
Diacetone alcohol	x	x	17	18
Diallyl hexahydrophthalate	—	x	33	30
Diallyl phathalate	x	x	27	24
N,N-Diamylacetamide	x	x	51	59
Dibutyl phthalate	x	x	33	32
Dibutyl sebacate	—	x	35	37
Dibutyl tartrate	—	x	19	18
N,*N*-Di-*n*-butyl-*p*-toluenesulfonamide	x	x	35	33

TABLE 5.23. *Continued*

MATERIAL	DETERMINED BY—		SOLUBILITY OF DDT	
	Synthetic method	Refractive index method	Per 100 ml. of solvent	Per 100 grams of solvent
	Individual Substances		*grams*	*grams*
o-Dichlorobenzene	x	x	59	45
Diethyl carbonate	—	x	42	43
Diethylene glycol monobutyl ether (Butyl Carbitol)	x	x	34	36
Diethylene glycol monobutyl ether acetate (Butyl Carbitol acetate)	x	x	34	35
Diethylene glycol monoethyl ether (Carbitol)	x	—	12	12
Diethylene glycol monoethyl ether acetate (Carbitol acetate)	x	x	33	33
Dimethyl phthalate	x	x	34	29
1,4-Dioxane	x	x	92	89
Diphenylmethane	x	x	36	36
m-Diisopropylbenzene	—	x	19	22
Dipropylene glycol	x	—	5	5
Di-*n*-propyl homophthalate	—	x	35	32
beta-Ethoxyethyl chloroacetate	x	—	22[1]	19[1]
beta-Ethoxyethyl phthalate	x	—	16	15
Ethyl acetoacetate	x	x	24	23
Ethyl alcohol (95 per cent)	x	—	2[1]	2[1]
Ethyl benzoate	x	x	57	54
Ethyl cinnamate	x	x	41	39
Ethylene dichloride	x	x	59	47
Ethylene glycol diacetate	—	7	19	17
Ethylene glycol monobenzyl ether (Benzyl Cellosolve)	x	x	14	13
Ethylene glycol monoethyl ether (Cellosolve)	x	x	19	17
Ethylene glycol monoethyl ether acetate (Cellosolve acetate)	x	x	40	36
Ethylene glycol monophenyl ether (Phenyl Cellosolve)	x	—	10	9
Ethyl ether	x	—	28[1]	39[1]
2-Ethyl-1,3-hexanediol (Rutgers' 612)	x	—	[1]	2[1]
Ethyl lactate	x	x	12	12
Ethyl oleate	—	x	17	20
Furfuryl alcohol	—	x	7	6
Hexahydroisothymol	x	x	6	7
Isophorone	x	x	74	80
Isopropyl alcohol	x	—	3[1]	4[1]
Isopropyl lactate	—	x	18	20
Lauric aldehyde	x	x	17	20

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[1] Approximate values only.

TABLE 5.23. *Continued*

MATERIAL	DETERMINED BY—		SOLUBILITY OF DDT	
	Synthetic method	Refractive index method	Per 100 ml. of solvent	Per 100 grams of solvent
	Individual Substance			
			grams	*grams*
Mesityl oxide	—	x	65	76
p-Methoxybenzyl alcohol	x	x	9	8
Methyl isobutyl ketone	x	x	47	59
Methylene chloride	x	—	88[1]	66[1]
Methyl alpha-naphthylacetate	x	x	35	31
Methyl alpha-naphthyl ether	x	x	48	44
Methyl isopropylcyclohexyl acetate	—	x	42	45
beta-(3,4-Methylisopropyl)-phenoxy-beta'-chloroethyl ether	—	x	25	24
Methyl salicylate	x	x	40	34
Morpholine	x	x	75[2]	75[2]
Nitroethane	x	x	27	26
1-Nitropropane	x	x	34	34
2-Nitropropane	x	x	40	40
Oleic acid	x	—	8	9
2-Phenoxyethyl acetate	x	x	25	23
2-Phenylcyclohexanol	x	x	26	28
Phenyl ether	x	x	42	39
Propionic acid	x	x	16	16
Propylene glycol	x	—	<1	—
Safrole	x	x	39	36
Tetrachloroethane (acetylene tetrachloride)	x	—	61	38
Tetrachloroethylene	x	x	38	23
Tetrahydrofurfuryl alcohol	x	x	17	16
Tetrahydronaphthalene	x	x	61	63
Triacetin	—	x	10	9
Tributyl citrate	x	x	25	24
Tributyl phosphate	x	x	50	51
1,2,4-Trichlorobenzene	—	x	44	28
Trichlorocumene	x	x	32	25
1-Trichloroethane	x	—	52[1]	39[1]
Trichloroethylene	x	x	64	44
Triethanolamine	x	—	<1	—
Undecylenic acid	—	x	12	13
Undecylenaldehyde	x	—	20[1]	24[1]
gamma-Valerolactone	x	x	58	54
o-Xylene	—	x	57	66

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[2] Approximate value only; some evidence of either chemical change of DDT or solvate formation.

TABLE 5.23. *Continued*

MATERIAL	DETERMINED BY— Synthetic method	DETERMINED BY— Refractive index method	SOLUBILITY OF DDT Per 100 ml. of solvent	SOLUBILITY OF DDT Per 100 grams of solvent
	Individual Substances			
Aliphatic Petroleum Fractions				
			grams	*grams*
Gasoline	x	—	10	13
Gasoline (100 octane)	x	—	9	12
Stoddard solvent	x	x	9	12
Kerosene (regular run)	x	x	8–10[3]	10–12
Fuel oil, No. 1	x	x	8–11[3]	10–14
Fuel oil, No. 2	x	x	7–10[3]	8–12
Lubricating oil, SAE 30	x	—	5	6
Diol 55 (high-boiling, aliphatic petroleum fraction of narrow distillation range)	x	x	7	8
Kerosene (refined, fly-spray base)	x	x	4[4]	5
Transformer oil	x	—	4–6[5]	5–7
Aromatic Petroleum Fractions				
Amsco-solv D (about 65% aromatics)	x	x	29	34
Amsco-solv E (about 65% aromatics)	x	x	30	34
Amsco-solv F (about 76% aromatics)	x	x	33	38
Solvesso No. 1 (aromatic naphtha)	x	x	47	59
Solvesso No. 2 (aromatic naphtha)	—	x	46	54
Solvesso No. 3 (aromatic fraction, medium boiling range)	—	x	33	38
S/V Culicide Oil B or PD-428-G (chiefly methyl- and polymethylnaphthalenes)	x	—	48[1]	47[1]
PD-544-A (upper fraction of S/V Culicide Oil B)	x	x	40	39
PD-544-B (middle fraction of S/V Culicide Oil B)	x	x	45	46
PD-544-C, regular (lower fraction of S/V Culicide Oil B)	x	x	34	38
PD-544-B, treated	x	x	41	42
PD-544-C, broad fraction	—	x	38	42
PD-544-C, special, new fraction	x	x	44	48
Special fraction of S/V Culicide Oil B (similar to PD-544-B)	x	x	48	50
Solvent B-1819 (refined, high-boiling fraction of S/V Culicide Oil B)	—	x	50[1]	50[1]
Sovasol 73 (aromatic naphtha)	—	x	25	32

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[3] Range for samples from 2 sources.

[4] 5 samples from 4 manufacturers ranged from 3.7 to 4.5.

[5] Range for 4 samples.

TABLE 5.23. *Continued*

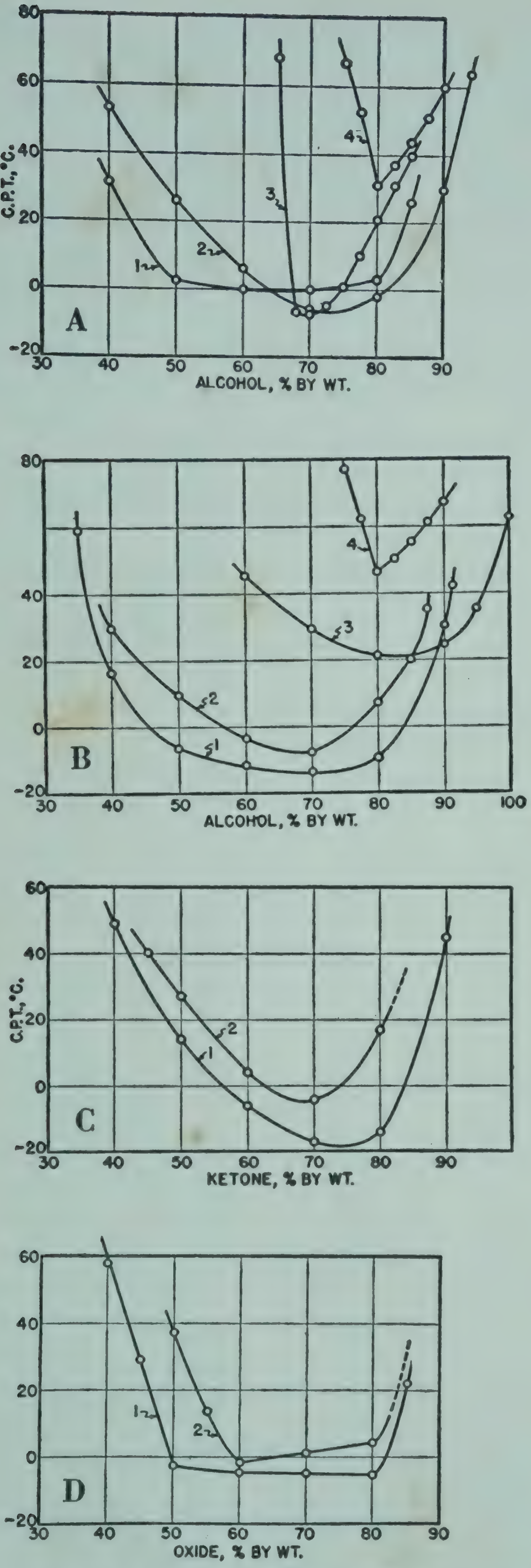
MATERIAL	DETERMINED BY—		SOLUBILITY OF DDT	
	Synthetic method	Refractive index method	Per 100 ml. of solvent	Per 100 grams of solvent
	Individual Substances			
			grams	*grams*
Sovasol 74 (aromatic naphtha)	—	x	42	50
Sovasol 75 (aromatic fraction, medium boiling range)	x	x	25	30
APS 202 (refined, high-boiling fraction of S/V Culicide Oil B)	—	x	45	44
Velsicol AR-40, July 1944 (chiefly monomethylnaphthalene)	x	x	48	51
Velsicol AR-40, monoethyl cut (chiefly monomethylnaphthalene)	x	x	59	61
Velsicol AR-50 (chiefly mono- and dimethylnaphthalenes)	—	x	55	56
Velsicol AR-60 (chiefly di- and trimethylnaphthalenes)	x	x	57	58
Velsicol NR-70 (chiefly tetramethylnaphthalene)	—	x	52	50
Coal-Tar Fractions				
Xylene, 10-degree	x	x	53	61
Solvent naphtha (industrial xylene)	x	x	52	60
Refined S.H. Solvent (light oil distillate, similar to solvent naphtha)	x	x	54	63
Hi-Flash solvent	x	x	48	55
Crude light solvent	x	x	58	66
Cumene fraction (chiefly pseudocumene)	x	x	42	48
Heavy solvent	x	x	58	62
Wire enamel solvent	x	x	60	64
Special heavy solvent	x	x	55	59
Pale yellow Hi-Flash solvent	—	x	39	45
Special fraction (Hi-Flash type)	x	x	32	37
K-327 (chiefly methylnaphthalenes)	x	x	67	66
Neutral oil	—	x	67	66
Kolineum (refined coal-tar creosote)	—	x	58	53
Special hydrocarbon oil	—	x	53	53
Hydrocarbon oil	—	x	70	71
Cresylic acid	—	x	17	17
Pine-Distillation Products				
Pine oil (Yarmor 302)	x	—	10	11
Pine oil (Yarmor 302W)	x	—	16	17
Turpentine, spirits	x	x	17	20
Pinene No. 111 (chiefly alpha-pinene)	—	x	14	16
Solvenol No. 1 (terpene hydrocarbons, chiefly dipentene)	—	x	22	26

TABLE 5.23. *Continued*

MATERIAL	DETERMINED BY—		SOLUBILITY OF DDT	
	Synthetic method	Refractive index method	Per 100 ml. of solvent	Per 100 grams of solvent
	Individual Substance			
			grams	*grams*
Dipentene No. 122 (terpene hydrocarbons, chiefly dipentene)	—	x	24	28
Terposol No. 3 (chiefly terpinyl methyl ethers)	x	x	21	23
Hercosol No. 80 (chiefly fenchone and camphor)	x	x	38	43
Hercolyn (chiefly hydrogenated methyl abietate)	—	x	21	20
Laksol (light distillate from pine wood)	x	x	62	72
DHS Activator (chiefl. ethylene glycol ether of pinene)	x	x	17	17
chiefly isobornyl thiocyanoacetate)	x	—	29	27
Miscellaneous				
Alox 152 (methyl esters of oxidized petroleum products)	x	—	9	10
Alox 800 (oxidized petroleum products)	x	x	18	19
Aroclor 1242 (chlorinated biphenyl)	x	x	48	35
Aroclor 1248 (chlorinated biphenyl)	x	—	30[1]	21[1]
Aroclor 1254 (chlorinated biphenyl)	x	—	12	8
Carbon Met (chlorinated coal-tar fraction)	x	x	49	51
Castor oil	x	x	7	7
Cottonseed oil	x	x	11	12
Dowtherm A (diphenyl oxide 74%, biphenyl 26%)	x	x	40	38
Dow Corning fluid, Type 200, vis. 500 cstks. (organic silicon polymer)	x	—	<1	—
Dow Corning fluid, Type 500, vis. 5 cstks. (organic silicon polymer)	x	—	<1	—
HB-40 (hydrogenated terphenyls)	x	x	24	24
Linseed oil, raw	x	x	11	12
Peanut oil	x	x	11	12
Phenol S (chiefly isopropyl cresols, byproduct from thymol)	x	—	7	7
Sesame oil	x	x	8	9
Triton B-1956 (polyglyceride of a glyptal resin)	x	x	9	9
Triton X-100 (polyethylene glycol alkyl aryl ether)	x	x	12	11
Tween-60 (sorbitan monostearate, polyoxyalkylene derivative)	x	x	14	13

TABLE 5.24. SOLUBILITIES OF ISOMERS OF BENZENE HEXACHLORIDE AT 20°

SOLVENTS	SOLUBILITY G./100 G. SOLUTION			
	Alpha	Beta	Gamma	Delta
Acetic acid, glacial	4.2	1.0	12.8	25.6
Acetone	13.9	10.3	43.5	71.1
Benzene	9.9	1.9	28.9	41.1
n-Butyl alcohol	1.6	0.7	4.4	19.4
n-Butyl acetate	10.8	7.1	31.5	54.4
iso-Butyl alcohol	0.9	0.4	3.0	13.5
Carbon tetrachloride	1.8	0.3	6.7	3.6
Chloroform	6.3	0.3	24.0	13.7
*Cyclo*hexane	1.4	0.8	4.6	2.7
*Cyclo*hexene	5.5	1.0	17.4	14.6
*Cyclo*hexanol	1.9	0.6	4.6	17.3
*Cyclo*hexanone	17.3	12.1	36.7	49.9
"Dec" (decahydronaphthalene)	2.5	0.4	8.7	10.4
Diacetone alcohol	5.4	2.9	21.0	30.5
Diethyl carbonate	10.2	4.1	28.4	46.3
Diesel oil	1.5	0.3	4.1	9.2
Dimethyl acetal	14.3	3.4	38.7	54.7
Dioxan	33.6	7.8	31.4	58.9
Ether	6.2	1.8	20.8	35.4
Ethyl alcohol	1.8	1.1	6.4	24.2
Ethyl acetate	12.7	6.9	35.7	58.5
Ethylene dichloride	7.9	0.6	28.9	27.3
Ethylene glycol	0.3	0.1	0.6	4.1
Ethylidene chloride	5.7	0.7	20.2	19.5
Glycerine	0.02	Nil	0.06	0.2
Methyl alcohol	2.3	1.6	7.4	27.3
Methyl acetate	13.6	6.7	27.7	62.1
Methyl propionate	13.0	7.9	37.8	61.6
Monochlorobenzene	7.4	0.4	23.4	21.4
Naphtha, heavy (230°–270°)	5.8	1.5	18.1	30.4
Odourless distillate (198°–257°)	0.8	0.02	2.0	1.1
Paraffin (138°–212°)	1.2	0.5	3.2	4.6
Perchloroethylene	2.4	0.1	7.4	3.5
Pentane	0.9	0.1	2.2	1.6
Petrol ether 40–60	0.7	0.1	2.1	1.6
" " 60–80	1.0	0.2	2.7	1.8
" " 80–100	1.0	0.2	2.9	3.2
" " 100–120	1.3	0.2	3.5	3.5
n-Propyl alcohol	1.6	1.1	5.2	21.1
iso-Propyl alcohol	0.6	0.4	2.8	18.0
Toluene	9.0	2.1	27.6	41.6
Trichloroethylene	3.7	0.3	14.7	7.6
Distilled water (parts per million)	(10)	(5)	(10)	(10)
White oil	0.7	0.02	1.9	1.1
Xylene	8.5	3.3	24.7	42.1



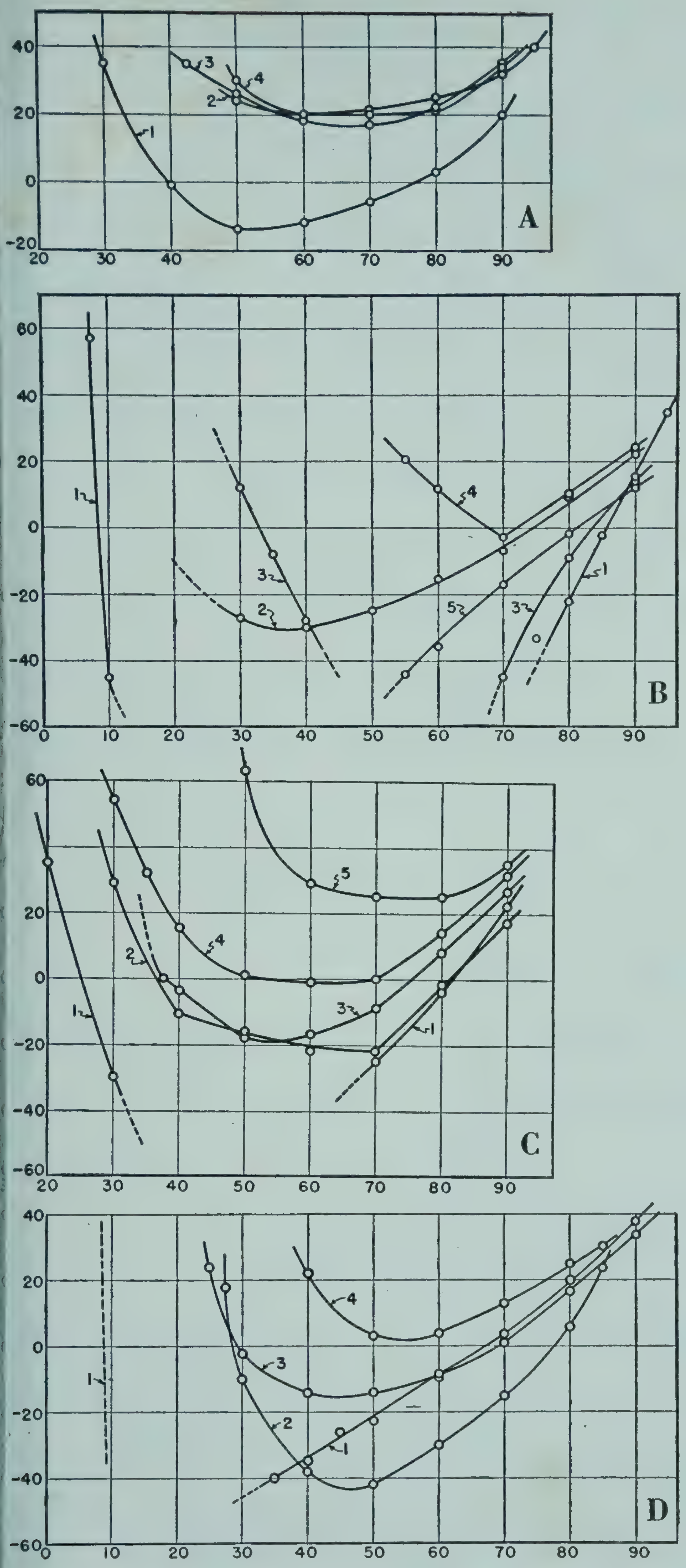
A. (1) *tert*-Butyl alcohol, (2) ethyl alcohol, (3) *sec*-butyl alcohol, (4(*n*-butyl alcohol

B. (1) *n*-Prophyl alcohol, (2) isopropyl alcohol, (3) methyl alcohol, (4) isobutyl Slcohol

C. (1) Acetonylacetone, (2) Acetone

D. (1) Dioxolene (2) Dioxane

Figure 5.9. Critical Peptization Temperature Curves for Commercial Zein in Binary Organic Solvents with Water as One Component.[39]



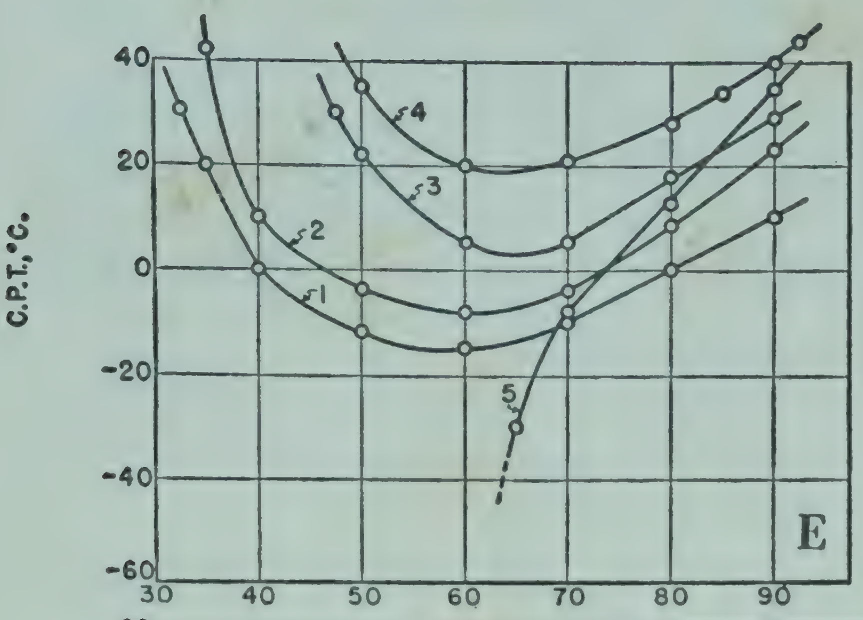
A. (1) Acetonylacetone, (2) acetone, (3) mesityl oxide, (4) methyl ethyl ketone

B. (1) Furfural, (2) acetaldehyde, (3) crotonaldehyde, (4) 2-ethyl-3-propylacrolein, (5) acetaldol

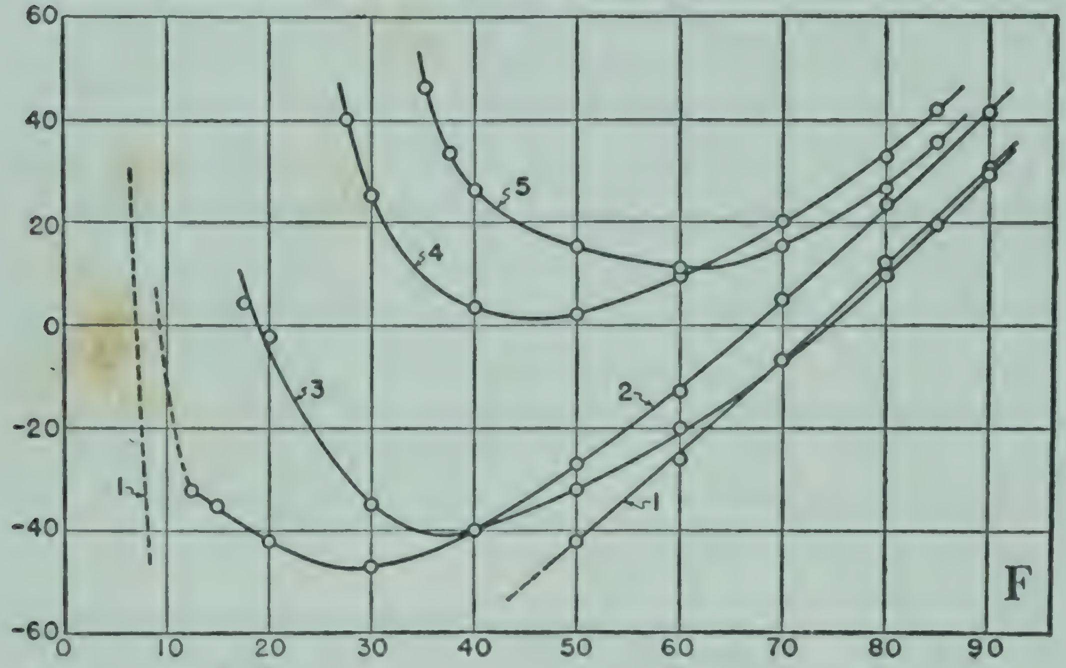
C. (1) Dioxolane, (2) dioxane, (3) propylene oxide, (4) isophorone, (5) phorone

D. (1) Chloroform, (2) *sym*-dichlorodiethyl ether, (3) propylene dichloride, (4) tetrachloroethylene

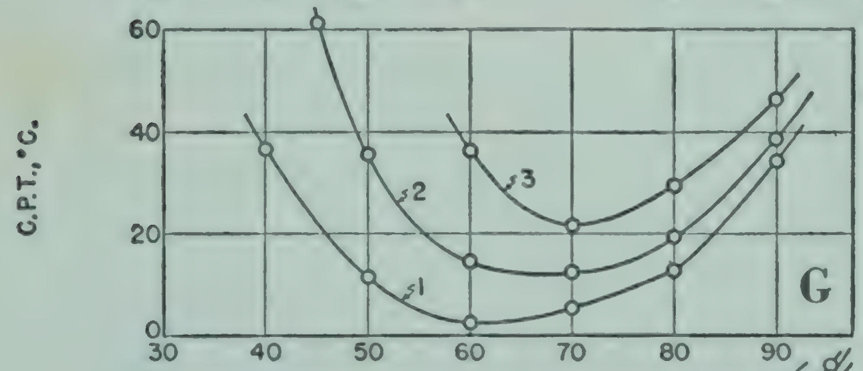
Figure 5.10. Critical Peptization Temperature Curves for Commercial Zein in Binary Organic Solvents with Methyl Alcohol as One Component.[39]



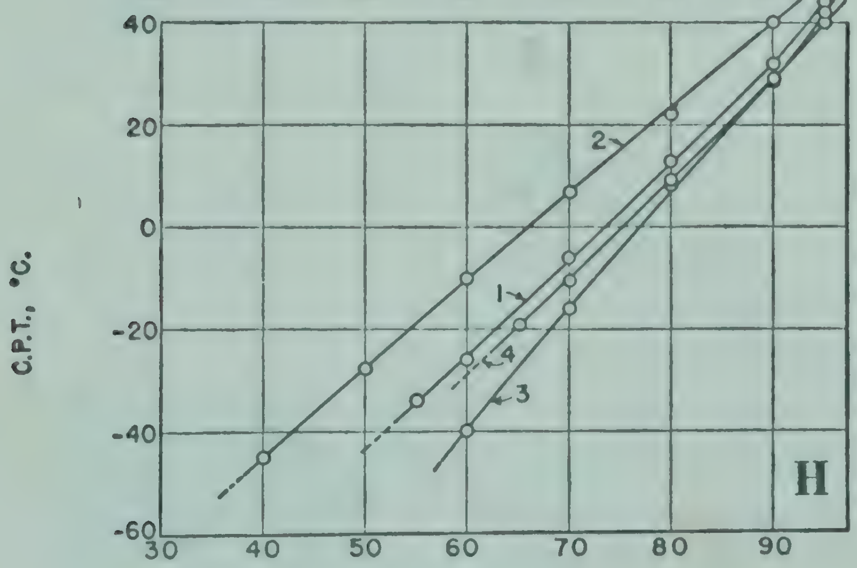
E. (1) Methyl acetoacetate, (2) ethylacetoacetate, (3) ethyl malonate, (4) ethyl formate, (5) butyl lactate 95% (technical)



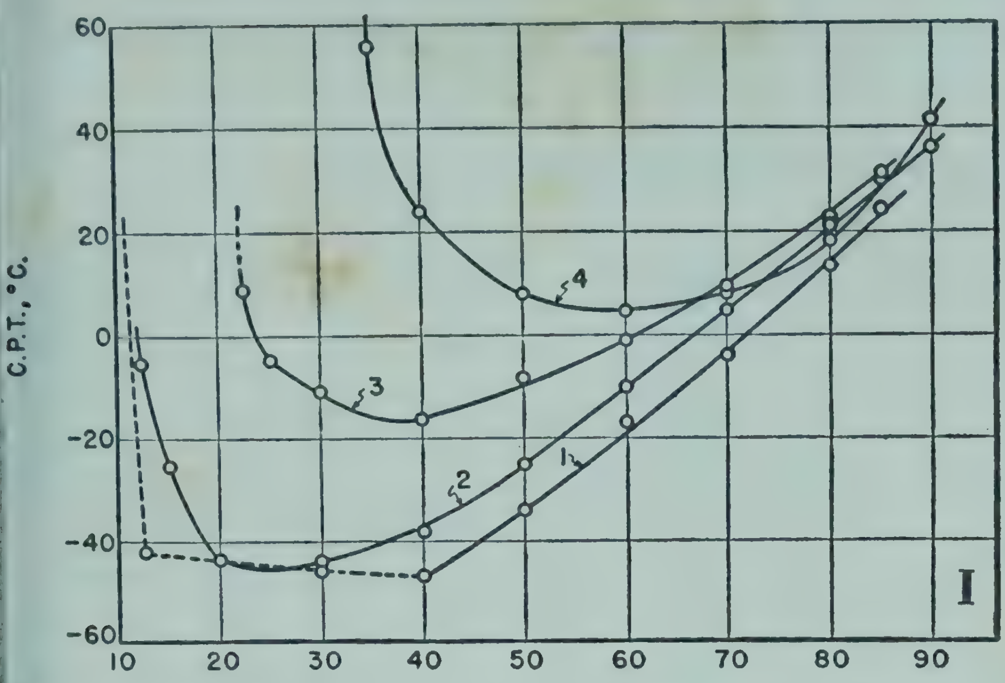
F. (1) *sym*-Tetrachloroethane, (2) pentachloroethane (3) ethylene dichloride, (4) carbon tetrachloride, (5) dichloropentane



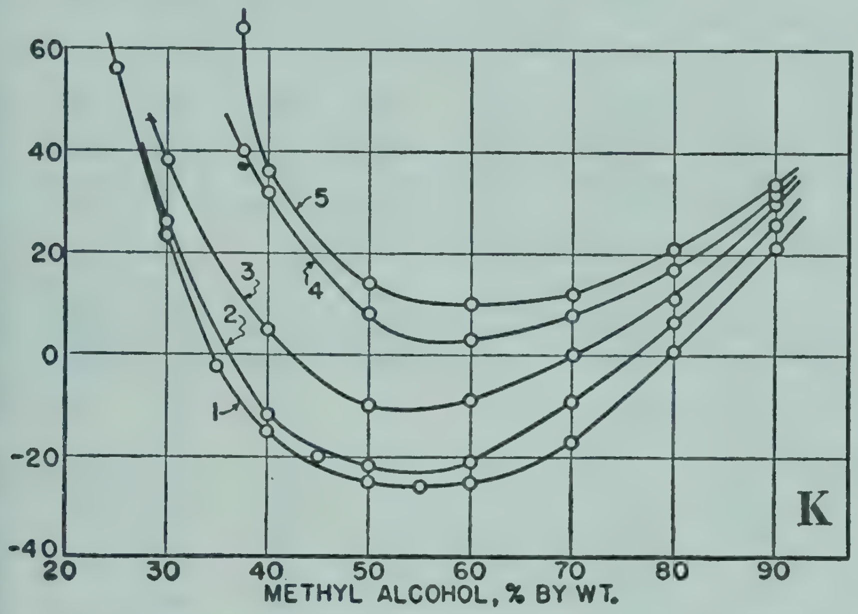
G. (1) Benzene, (2) toluene, (3) *m*-xylene



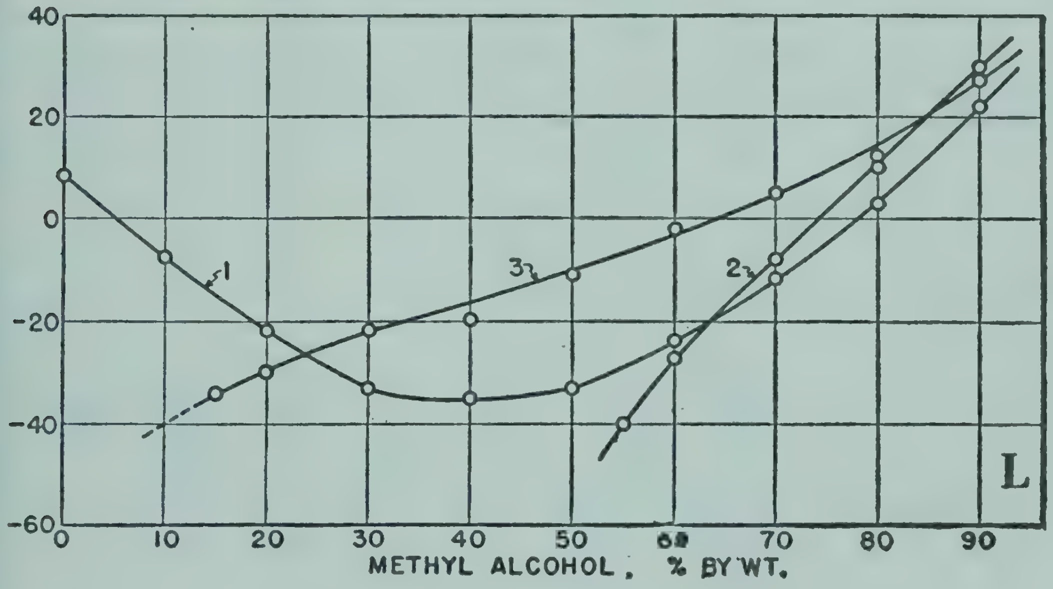
H. (1) Methyl "Cellosolve," (2) "Cellosolve," (3) methyl "Carbitol," (4) "Cartibol"



I. (1) β-Trichloroethane, (2) methylene chloride, (3) trichlorethylene, (4) *sym*-dichloroisopropyl ether



K. (1) Nitromethane, (2) nitroethane, (3) 1-nitropropane, (4) 2-nitropropane, (5) 2-nitrobutane



L. (1) Ethylene glycol, (2) diethylene glycol, (3) propylene glycol

TABLE 5.25. SOLUBILITY OF HALOGENATED METHANES IN ORGANIC SOLVENTS[37]

	CCl_2F_2		CCl_3F		$CHCl_2F$		CH_2Cl_2	
Solvents	G./g.	Mole fr.	G./g.	Mole fr.	G./g.	Mole fr.	G./g.	Mole fr.
Theoretical		0.453		0.356		0.381		0.311
Alcohols and Ethers								
n-Hexyl alcohol, $C_6H_{13}OH$	0.291	0.197	0.287	0.176	0.425	0.296		
Cyclohexanol, $C_6H_{11}OH$	.170	.123	.229	.143	.388	.274		
Phenol, C_6H_5OH	Very low		Very low		.269	.197	0.210	0.130
Ethylene glycol, $HOCH_2CH_2OH$	.0118	.00602	.0150	.00677	.100	.055		
Trimethylene glycol, $HOCH_2CH_2CH_2OH$	.0223	.0138	.0309	.0168	.106	.073		
Cyclohexyl methyl ether, $C_6H_{11}OCH_3$	.648	.380	.637	.346	.900	.498		
Anisole, $C_6H_5OCH_3$	.318	.220	.415	.244	.673	.415	.385	.328
Tetraethylene glycol dimethyl ether, $CH_3O(CH_2CH_2O)_4CH_3$	.223	.290	.312	.336	1.110	.706	.580	.602
Acids and Esters								
Acetic acid, CH_3COOH	.310	.133	.251	.0986	.688	.286	.280	.174
Propionic acid, C_2H_5COOH	.467	.223	.420	.185	.665	.330	.320	.218
Ethyl laurate, $C_{11}H_{23}COOC_2H_5$	.399	.430	.420	.412	.561	.556		
Ethyl caprylate, $C_7H_{15}COOC_2H_5$	.480	.406	.474	.373	.754	.557		
Aldehydes and Ketones								
Heptaldehyde, $C_6H_{13}CHO$	.525	.327	.534	.304	.979	.519	.473	.388
Cyclohexanone, $C_6H_{10}O$	.381	.236	.486	.257	1.278	.548	.630	.421
Acetylacetone, $CH_3COCH_2COCH_3$	.386	.242	.400	.226	1.023	.499	.455	.394
Acetonylacetone, $CH_3COCH_2CH_2COCH_3$	.185	.147	.247	.170	1.163	.563	.572	.434
Nitrogen Compounds								
Cyclohexylamine, $C_6H_{11}NH_2$	.581	.322			1.070	.506	.520	.377
Aniline, $C_6H_5NH_2$	.0604	.0442	.113	.0706	.385	.258		
Dimethylcyclohexylamine, $C_6H_{11}N(CH_3)_2$	.576	.377	.640	.372	.807	.500		
Dimethylaniline, $C_6H_5N(CH_3)_2$	.262	.208	.382	.252	.695	.425		
Quinoline, C_9H_7N	.119	.113	.229	.177	.633	.443		
Acetamide, CH_3CONH_2	Very low		Very low		Very low		Very low	
N-Methylacetamide, $CH_3CONHCH_3$	.181	.0984	.256	.120	.955	.403	.427	.269
N,N-Dimethylacetamide, $CH_3CON(CH_3)_2$	.305	.180	.326	.171	1.870	.614	1.808	.452
Valeronitrile, C_4H_9CN	.470	.245			1.280	.550	0.630	.351
Benzonitrile, C_6H_5CN					.783	.438		
Nitrobutane, $C_4H_9NO_2$			.356	.210	.780	.438		
Nitrobenzene, $C_6H_5NO_2$					.471	.360		
Ethylmethylketoxime, $C_2H_5(CH_3)C{=}NOH$	.327	.190	.352	.182	.650	.338	.315	.244
Hydrocarbons and Bromides								
n-Decane, $C_{10}H_{22}$	.602	.415	.537	.357	.324	.309		
Mesitylene, $C_6H_3(CH_3)_3$	.532	.346	.568	.332	.668	.437	.328	.317
Bromobenzene, C_6H_5Br	.210	.214	.299	.255	.335	.338		
n-Hexyl bromide, $C_6H_{13}Br$	.367	.333	.396	.322	.398	.390		

Analytical Chemistry:

Organic solvents are now bidding for attention in the field of analytical chemistry. Ethyl alcohol has been used as a titration medium in determining either the acidity of alkalinity of substances which are insoluble in water. More recently *n*-butyl alcohol, amyl alcohol, "Cellosolve" solvents,

TABLE 5.26. SOLUBILITY OF MONOFLUORODICHLOROMETHANE IN ORGANIC SOLVENTS[37]

Theoretical or "Ideal" mole fraction in saturated solution 0.381

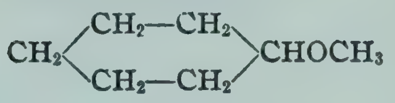
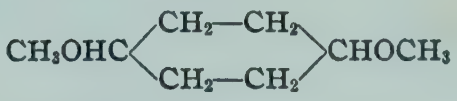
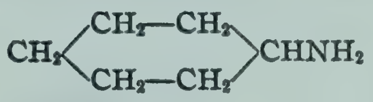
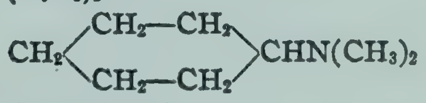
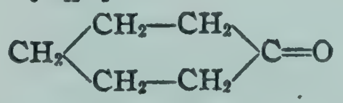
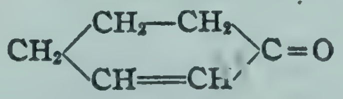
	Formula	Solubility	
		G./g.	Mole fr.
	Alcohols and Ethers		
Phenol	C_6H_5OH	0.269	0.197
Ethylene glycol	$HOCH_2CH_2OH$	.10	.055
Trimethylene glycol	$HOCH_2CH_2CH_2OH$	.106	.073
Anisole	$C_6H_5OCH_3$	.673	.415
Phenetole	$C_6H_5OC_2H_5$	.625	.425
Phenyl vinyl ether	$C_6H_5OCH{=}CH_2$	.559	.394
Dimethyl ether of ethylene glycol	$CH_3OCH_2CH_2OCH_3$	1.55	.576
Cyclohexyl methyl ether		0.900	.500
1,4-Dimethoxycyclohexane		0.941	.571
	Acids and Esters		
Acetic acid	CH_3COOH	0.688	0.286
Propionic acid	C_2H_5COOH	.665	.330
n-Butyl butyrate	$CH_3(CH_2)_2COO(CH_2)_3CH_3$	.870	.546
Diethyl oxalate	$C_2H_5OCOCOOC_2H_5$	.561	.556
Dimethyl sulfate	$(CH_3O)_2SO_2$	.463	.361
Triethyl phosphate	$(C_2H_5O)_3PO$	1.132	.666
Tributyl phosphate	$(C_4H_9O)_3PO$	0.842	.685
Tri-(β-methoxyethyl) phosphate	$(CH_3OCH_2CH_2O)_3PO$	.836	.687
	Amines and Substituted Amines		
Cyclohexylamine		1.070	0.506
Aniline	$C_6H_5NH_2$	0.385	.258
Quinoline	C_9H_7N	.633	.443
Diphenylamine	$(C_6H_5)_2NH$	(Very low)	...
Dimethylcyclohexylamine		0.807	.500
Dimethylaniline	$C_6H_5N(CH_3)_2$	.695	.425
Methyldiphenylamine	$(C_6H_5)_2NCH_3$	.357	.388
	Amides and Substituted Amides		
Formamide	$HCONH_2$	0.075	0.032
Acetamide	CH_3CONH_2	(Very low)	...
Methylformamide	$HCONHCH_3$	0.768	.303
N,N-Dimethylformamide	$HCON(CH_3)_2$	.931	.398
N-Methylacetamide	$CH_3CONH(CH_3)$	.955	.403
N,N-Dimethylacetamide	$CH_3CON(CH_3)_2$	1.87	.614
N-Tetraethyloxamide	$[CON(C_2H_5)_2]_2$	0.965	.651
N,N-Tetramethylsuccinamide	$[CH_2CON(CH_3)_2]_2$	1.180	.663
N-Methyl-N-cyclohexylacetamide	$CH_3CON(CH_3)C_6H_{10}$	1.140	.632
	Aldehydes and Ketones		
Benzaldehyde	C_6H_5CHO	0.750	0.436
Heptaldehyde	$C_6H_{13}CHO$	.979	.519
Paraldehyde	$C_6H_{12}O_3$	.888	.532
Cyclohexanone		1.278	.548
Δ^2-Cyclohexenone		0.903	.457
Acetylacetone	$CH_3\underset{O}{\underset{\|}{C}}CH_2\underset{O}{\underset{\|}{C}}CH_3$	1.023	.499

TABLE 5.27. SOLUBILITY OF METHYLENE CHLORIDE IN ORGANIC SOLVENTS[37]

(Theoretical or "Ideal" Mole Fraction in Saturated Solution 0.311)

		Solubility	
	Formula	G./g.	Mole fr.
	Alcohols and Ethers		
Phenol	C_6H_5OH	0.210	0.130
Anisole	$C_6H_5OCH_3$	.385	.328
1,4-Dimethoxycyclohexane	$C_6H_{10}(OCH_3)_2$	.460	.442
Diethyl ether of diethylene glycol	$C_2H_5O(CH_2CH_2O)_2C_2H_5$	.568	.520
Dimethyl ether of tetraethylene glycol	$CH_3O(CH_2CH_2O)_4CH_3$	.580	.602
	Acids and Esters		
Acetic acid	CH_3COOH	0.280	0.174
Propionic acid	C_2H_5COOH	.320	.218
Triethyl phosphate	$(C_2H_5)_3PO_4$	.55	.541
Tri-*n*-propyl phosphate	$(C_3H_7)_3PO_4$	.50	.567
Tri-*n*-butyl phosphate	$(C_4H_9)_3PO_4$	.435	.574
Triphenyl phosphite	$(C_6H_5)_3PO_3$	.192	.412
Tri-*o*-cresol phosphate	$(C_6H_4OCH_3)_3PO_4$	.213	.470
Ethyl ether of diethylene glycol acetate	$C_2H_5O(CH_2CH_2O)_2COCH_3$	.500	.509
Ethyl acetoacetate	$CH_3COCH_2COOC_2H_5$	.454	.410
Ethyl diethylacetoacetate	$CH_3COC(C_2H_5)_2COOC_2H_5$	.403	.468
	Amines, Amides and Oximes		
Cyclohexylamine	$C_6H_{11}NH_2$	0.520	0.377
Diphenylamine	$(C_6H_5)_2NH$	Very low	...
Formamide	$HCONH_2$	0.062	.038
Methylformamide	$HCONHCH_3$	.365	.202
Dimethylformamide	$HCON(CH_3)_2$	.410	.261
Acetamide	CH_3CONH_2	Very low	...
N-Methylacetamide	$CH_3CONHCH_3$	0.427	.269
N,N-Dimethylacetamide	$CH_3CON(CH_3)_2$	.808	.452
N-Methyl-N-cyclohexyl-*n*-butanesulfonamide	$C_4H_9SO_2N(CH_3)C_6H_{11}$	.351	.490
N-Methyl-N-cyclohexylacetamide	$C_6H_{11}N(COCH_3)CH_3$	.600	.521
N-Ethyl-N-cyclohexylacetamide	$C_6H_{11}N(COCH_3)C_2H_5$	.565	.530
Ethyl methyl ketoxime	$C_2H_5(CH_3)C{=}NOH$	.315	.244
	Aldehydes and Ketones		
Benzaldehyde	C_6H_5CHO	0.430	0.349
Salicylaldehyde	$o\text{-}C_6H_4(OH)CHO$	.320	.315
Heptaldehyde	$CH_3(CH_2)_5CHO$	.473	.388
Paraldehyde	$C_6H_{12}O_3$	.385	.374
Cyclohexanone	$C_6H_{10}O$	.630	.421
Δ^2-Cyclohexenone	C_6H_8O	.473	.349
Acetylacetone	$CH_3COCH_2COCH_3$	.455	.394
Acetonylacetone	$CH_3COCH_2CH_2COCH_3$	.572	.434

acetone, and 1,4-dioxane have been used for this purpose. Ruehle[40] has developed several potentiometric titrations in non-aqueous solutions; the results of his work are portrayed in Figs. 5.11 to 5.13 (page 189).

TABLE 5.27a

Acceptor	Donor	Heat of mixing per mole of soln. at 3° cal.
$CHCl_3$	n-$C_4H_9NH_2$	700
$CHCl_3$	$C_6H_{11}NH_2$	800
$CHCl_3$	$C_6H_{11}N(CH_3)_2$	1166
$CHCl_3$	$C_6H_5N(CH_3)_2$	280
$CHCl_3$	$CH_3CON(CH_3)_2$	920
$CHCl_3$	$C_6H_5CON(C_2H_5)_2$	1090
$CHCl_3$	n-C_4H_9CN	390
$CHCl_3$	C_6H_5CN	297
$CHCl_3$	$CN(CH_2)_3CN$	233
$CHCl_3$	$CN(CH_2)_3CN$	253
$CHCl_3$	$CN(CH_2)_3CN$	261
$CHCl_3$	$C_6H_5NO_2$	118
$CHCl_3$	$C_2H_5ONO_2$	113
$CHCl_3$	CH_3NO_2	None
$CHCl_3$	$C_6H_5OCH_3$	175
$CHCl_3$	$C_6H_{11}OCH_3$	665
$CHCl_3$	$(C_2H_5)_2O$	700
$CHCl_3$	CH_3COCH_3	495
$CHCl_3$	$CH_3CO_2C_2H_5$	544
$CHCl_3$	$C_6H_5SO_3C_2H_5$	249
$CHCl_3$	$C_6H_5SO_3C_2H_5$	285
$CHCl_3$	$C_6H_5SO_3C_2H_5$	270
$CHCl_3$	$(C_2H_5O)_2SO_2$	257
$CHBr_3$	C_5H_5N	498
$CHBr_3$	$CH_3CON(CH_3)_2$	918
$CHBr_3$	$CH_3CON(CH_3)_2$	901
$CHBr_3$	$(C_2H_5)_2O$	515
$CHBr_3$	CH_3COCH_3	342
CH_2Cl_2	$CH_3CON(CH_3)_2$	527
CH_2Cl_2	$(C_2H_5)_2O$	245
CH_2Br_2	$CH_3CON(CH_3)_2$	400
CH_2Br_2	$(C_2H_5)_2O$	200
CH_2I_2	$CH_3CON(CH_3)_2$	100
CH_2I_2	$(C_2H_5)_2O$	None
$C_6H_5CHCl_2$	$CH_3CON(CH_3)_2$	426
$C_6H_5CHCl_2$	$CH_3CON(CH_3)_2$	500
$C_6H_5CHCl_2$	$(C_2H_5)_2O$	232
$C_6H_5CHCl_2$	CH_3COCH_3	200
$(C_6H_5)_2CHCl$	$CH_3CON(CH_3)_2$	208
$(C_6H_5)_2CHCl$	$(C_2H_5)_2O$	Very sl.
$HCCl_2CCl_2H$	C_5H_5N	589
$HCCl_2CCl_2H$	C_5H_5N	605
$HCCl_2CCl_2H$	C_6H_5CN	362
$HCCl_2CCl_2H$	$C_6H_5NO_2$	140
$HCCl_2CCl_2H$	C_6H_6	125
$HCCl_2CCl_2H$	CH_3COCH_3	610
$HCCl_2CCl_2H$	CH_3COCH_3	610
$HCCl_2CCl_2H$	$CH_3CO_2C_2H_5$	608
$HCCl_2CCl_2H$	$CH_3CO_2C_2H_5$	572
$CCl_2{=}CHCl$	$CH_3CON(CH_3)_2$	212
$CCl_2{=}CHCl$	$C_6H_5NO_2$	None
$CCl_2{=}CHCl$	C_6H_6	None
$CCl_2{=}CHCl$	$(C_2H_5)_2O$	278
$CCl_2{=}CCl_2$	$CH_3CON(CH_3)_2$	None
$CCl_2{=}CCl_2$	$(C_2H_5)_2O$	None
$C_6H_5CCl_3$	$CH_3CON(CH_3)_2$	249
$C_6H_5CCl_3$	$CH_3CON(CH_3)_2$	305
$C_6H_5CF_3$	$CH_3CON(CH_3)_2$	120
CH_3NO_2	$CH_3CON(CH_3)_2$	118
$HC(OC_2H_5)_3$	$CH_3CON(CH_3)_2$	Sl. cooling
$HC(OC_2H_5)_3$	n-C_6H_{14}	Cooling
$CH_2(OC_2H_5)_2$	$CH_3CON(CH_3)_2$	Sl. cooling
$CH_2(OC_2H_5)_2$	n-C_6H_{14}	Cooling

TABLE 5.28. ZEIN SOLVENTS[39]

Solvent	Critical Peptization Temp., ° C.
Acetamide	82
Acetic acid	14
2-Amino-2-ethyl-1,3-propanediol[a]	38
2-Amino-2-methyl-1-propanol[a]	24
2-Amino-2-methyl-1,3-propanediol[a]	>109 (m. p.)
o-Aminophenol[b]	>173 (m. p.)
m-Aminophenol[b]	>122 (m. p.)
Aniline	Gels
Benzyl alcohol[b]	−18
Benzyl Cellosolve[c]	<−40
Butylamine[d]	<−40
Butyl tartrate	<−40
1,3-Butylene glycol[c]	39
o-Cyclohexylphenol[b]	>55 (m. p.)
1,3-Diaminopropanol[b]	40
Di[-β-hydroxyethyl]aniline[b]	>59 (m. p.)
Diethanolamine[c]	30
Diethylene glycol[c]	<−40
Diethylene glycol monoethyl ether (Carbitol)[c]	<−40
Diethylene glycol monomethyl ether (methyl Carbitol)[c]	<−40
Diethylenetriamine[c]	<−40
Diglycol chlorohydrin[c]	<−40
Diisopropanolamine[c]	32
Diphenylquanidine[b]	>148 (m. p.)
s-Diphenylthiourea[b]	>154 (m. p.)
Dipropylene glycol[c]	<−40
Ethyl ether tripropylene glycol[c]	<−20
Ethyl lactate[e]	−24
Ethylphenylethanolamine[c]	<−25
Ethylene chlorohydrin[c]	<−40
Ethylene glycol[c]	18
Ethylene glycol monoethyl ether (Cellosolve)[c]	<−40
Ethylene glycol monomethyl ether (methyl Cellosolve)[c]	<−40
Ethylenediamine[c]	11
Formic acid[b]	7
Furfuryl alcohol[f]	<−40
Glycerol	139
Glycerol furfural[g]	<−40
Glyceryl-α,γ-dichlorohydrin[g]	<−40
Glyceryl-α,γ-dimethyl ether[g]	<−40
Glyceryl-α-monochlorohydrin[g]	<−40
Glyceryl-α-methyl ether[g]	<−40
Glyceryl-α-phenyl ether[g]	>54 (m. p.)
β-Hydroxyethylaniline[b]	<−30
Hydroxyethylethylenediamine[b]	<−40
2-Hydroxymethyl-1,3-dioxolane[c]	<−40
Lactic acid	<−40
Methyl alcohol	63
Methyl lactate[a]	<−40
Monoethanolamine[c]	6
Monoisopropanolamine[c]	−4
Morpholine[c]	−6
Morpholine ethanol[c]	>2 (m. p.)
Phenol	40
Phenyl Cellosolve[c]	<−40
Phenyldiethanolamine[c]	>56 (m. p.)
Phenylethanolamine[c]	−15
Propionic acid[b]	60 ±
Propylene chlorohydrin[c]	<−30
Propylenediamine[c]	<−40
Propylene glycol[c]	<−40
Pyridine	<−40
Resorcinol monoacetate[b]	0
Triethanolamine[c]	>21 (m. p.)
Triethylenetetramine[c]	<−40
Tetrahydrofurfuryl alcohol[f]	<−40
Triethylene glycol[c]	<−40
Triisopropanolamine[c]	>46 (m. p.)
Trimethylaminomethane[a]	>166 (m. p.)

[a] Commercial Solvents Corporation
[b] Eastman Kodak Company
[c] Carbide and Carbon Chemicals Corporation
[d] Sharples Chemicals Inc.
[e] American Cyanamid and Chemical Corporation
[f] Quaker Oats Company
[g] Glycerine Producers Association.

TABLE 5.29. SOLUBILITY OF MISCELLANEOUS SUBSTANCES

SH Soluble when hot
S Soluble
I Insoluble
P Partly soluble
SC Soluble but cloudy
SS Slightly soluble
G Gelled
OS Has selective solvent action for oil over wax

Solvents	Anthracene	Blown castor oil	Calcium resinate	Carbazol	Castor oil	Essential oils	Fats	Greases	Indene	Inglewood crude petroleum	Lead linoleate	Linseed oil	Manganese resinate	Mineral oil (tech. white)	Pennsylvania oil	Phenanthrene	Texas oil	Tricresyl phosphate	Tung oil	Zinc resinate	Pyrethrum (extract)
Acetal										S											
Acetaldehyde										P											
Acetone	SS			SH	S	S				P		S		I		S			S		
Acetophenone										P											
Amyl acetate			S			S					SS	S	S		OS		S	OS		S	
sec-Amyl acetate		S							S												
Amyl acetate (mixed isomers)		S							S												
Amyl acetate (from fusel oil)		S							S												
n-Amyl alcohol			S			S				S	SS	S	S		OS		S	OS		S	
sec-Amyl alcohol		S							I												
tert-Amyl alcohol										S											
Amyl alcohol (mixed isomers)		S							I												
Amyl alcohol (from fusel oil)		S							I												
Amyl lactate		S							P												
Amylene dichloride																					S
Benzene (nitrated pure)	SS			SS			S	P								SH					S
Benzene (industrial)	SS			SS			S	P								SH					S
Benzene (90% industrial)	SS			SS			S	P								SH					S
Benzene (B-refined)	SS			SS			S	P								SH					S
Butaldehyde										S					OS		OS				
n-Butyl acetate		S	S			S			S		SS	S	S		OS		OS			S	
sec-Butyl acetate		S							S												
n-Butyl alcohol		S	S			S			I		SS	S	SS		OS		OS			S	S
sec-Butyl alcohol		S							I	S											S
tert-Butyl alcohol																					S
Butyl butyrate			SS			S					SS	S	SS							S	
Butyl Carbitol												S									
Butyl "Cellosolve"		S							P			S			OS		OS				
Butyl lactate		S							P												
Carbon disulfide	SS			SS												SS					
Carbon tetrachloride	SS			SS						P						S					S
"Cellosolve"		S	S			S			P		SS	S	S		OS		OS			S	
"Cellosolve" acetate		S	S			S			S		I	S	S							S	
Chlorbenzene															OS		OS				
Chloroform	SS			SS						P						S					S

TABLE 5.29. SOLUBILITY OF MISCELLANEOUS SUBSTANCES—*Continued*

Solvents	Anthracene	Blown castor oil	Calcium resinate	Carbazol	Castor oil	Essential oils	Fats	Greases	Indene	Inglewood crude petroleum	Lead linoleate	Linseed oil	Manganese resinate	Mineral oil (tech. white)	Pennsylvania oil	Phenanthrene	Texas oil	Tricresyl phosphate	Tung oil	Zinc resinate	Pyrethrum (extract)
Diacetone alcohol			SS			S				I	SS	S	SS		OS		OS			S	
Dibutyl phthalate												S			OS		OS				
Dichlor ethyl ether			I			S					I	S	SS							S	
Diethylene glycol										I		SS									
Dimethyl phthalate												S									
Dioxane												S									
Ethyl acetate (pure 85%)		S							S	S		S			OS		OS				
Ethyl alcohol			SS			I			I		I	I	SS							SS	S
Ethyl alcohol (anhydrous)		S	SS			I			I		I	I	SS		OS		OS			SS	S
Ethyl ether	SS		S	SS		S				S	SS	S	SS			S				S	
Ethyl ether of diethylene glycol												S									
Ethyl lactate		S	S			S			P		SS	S	S							S	
Ethyl methyl ketone										S					OS		OS				
Ethylene dichloride			S			S				S	SS	S	S		OS		OS			S	S
Ethylene glycol										P		SS									
Furan										S											
Gasoline	SS			SS												SS					
Glycerin										P											
Glyceryl diacetate										I											
Glycol diacetate			I			S				I	I	I	SS							SS	
Hexalin										S											
n-Hexanol												S									
Hexone		S							S												
2-50-W. Hi-Flash naphtha	SS			SS			S	P								S					
Hi-Flash naphtha (yellow)	SS			SS			S	P								S					
Hydrogenated naphtha	SS			SS			S	P								S					
Isoamyl acetate										S											
Isoamyl alcohol										S											
Isopropyl acetate		S							S			S									
Isopropyl alcohol		S							I	I		SS			OS		OS				S
Isopropyl ether												S									
Kerosene															OS		OS				

TABLE 5.29.—*Continued*

Mesityl oxide												OS		OS		
Methanol		I						I	I	SS						S
Methyl acetate		S						S	I	S						
Methyl amyl acetate		S						S		S						
Methyl amyl alcohol		S						I		S						
Methyl amyl ketone				S	S				S	S	S				S	
Methyl butyl ketone				S	S					S	S				S	
Methyl "Carbitol"										SS						
Methyl "Cellosolve"										SH		OS		OS		
Methyl ethyl ketone		S		S	S			S		S	S				S	
Methyl isobutyl ketone (Hexone)										S						
Methyl isopropyl ketone		S						S								
Methyl propyl ketone		S		S	S			S		S	S				S	
Naphtha	SS		SS			S	P						S			
Naphtha (heavy)	SS		SS			S	P						S			
Naphtha (nitrated)	SS		SS			S	P						S			
3-B X naphtha	SS		SS			S	P						S			
2-10 M naphtha	SS		SS			S	P						S			
V. M. & P. naphtha	SS		SS			S	P						S			
Octyl acetate		S						S		S						
Octyl alcohol		S						I		S						
n-Propyl acetate		S						S								
n-Propyl alcohol		S						I				OS		OS		
Propylene dichloride										S						
Propylene glycol										SS						
Propylene oxide										S						
Pyridine	SS		S										S			
Quinoline									S							
Solvesso No. 1		I						S								
Tetralin									S							
Toluene (nitrated)	SS	S	SS			S	P	S				OS	S	OS		
Toluene (industrial pure)	SS	S	SS			S	P	S				OS	S	OS		
Toluene (90/120)	SS	S	SS			S	P	S				OS	S	OS		
Trichlorethylene										S						
Triethylene glycol										SS						
Troluoil		I						I								
Turpentine												OS		OS		
Xylene (5 degrees)		S				S	P	S				OS		OS		S
Xylene (10 degrees)		S				S	P	S				OS		OS		S
Xylene (industrial)		S				S	P	S				OS		OS		S

TABLE 5.30. SOLUBILITY OF GUMS

SH	Soluble when hot	I	Insoluble	G	Gelled
VS	Very soluble	P	Partly soluble	IG	Insoluble-gelled
S	Soluble	SC	Soluble but cloudy	SSH	Slightly soluble when hot
		SS	Slightly soluble		

Solvents	Asphalt petroleum	Gum camphor	Gum congo	Gum copal	Gum dammar	Gum dammar (dewaxed)	Gum dammar (whole)	Gum elemi	Gum guaiac	Gum kauri	Gum kauri (chips)	Gum manila	Gum mastic	Gum pontianac (nubs)	Gum rosin	Gum rosin "E"	Gum rosin ester	Gum sandarac	Gum tragacanth	Gum zanzibar
Acetone						S	P			P	S	S		S	S	S	P			
Acetophenone																				
Amyl acetate		S		S	I			S	SS	S			S			S	S	S	I	S
sec-Amyl acetate						S				P		P					S			
Amyl acetate (mixed isomers)						S				I		S					S			
Amyl acetate (from fusel oil)						S				P		P					S			
n-Amyl alcohol		S		S	I			SS	I	S			S			S	S	S	I	S
sec-Amyl alcohol						P				P		P					P			
Amyl alcohol (mixed isomers)						S				I		P					S			
Amyl alcohol (from fusel oil)						P				P		P					P			
Amyl chloride																				
Amyl lactate						S				I		P					S			
Benzene (nitrated pure)	S		I		I			S		I		I					S			
Benzene (industrial)	S		I		I			S		I		I					S			
Benzene (90% industrial)	S		I		I			S		I		I					S			
Benzene (B-refined)	S		I		I			S		I		I					S			
Brombenzene																				
Butyl acetate, 85%		S		SS	S	SC		S	I	S		SC	S			S	S	I	I	I
n-Butyl acetate		S		SS	S	SC		S	I	S		SC	S			S	S	I	I	I
sec-Butyl acetate						S				P		P					S			
n-Butyl alcohol						SC				S		P				S	S			
sec-Butyl alcohol						I				P		P					P			
tert-Butyl alcohol																				
Butyl butyrate		S		I	S			S	I	SS			S			S	S	I	I	I
Butyl "Carbitol"						P				S						S	P			
Butyl "Cellosolve"						S				S		P				S	S			
Butyl lactate						SC				P		P					S			
Butyric acid																				
Carbon disulfide																				
Carbon tetrachloride																				
"Cellosolve"		S		I	I	SC		SS	SS	P		SC	SS			S	S	S	I	S
"Cellosolve" acetate		S		I	I	SC		SS	SS	P		P	SS			S	S	S	I	I
Chloroform																				
Cyclochlorohexanes																				

Diacetone alcohol		S		S	I				SS	S			S			S	SS	S	I	SS
Dibutyl phthalate						S				S						S	S			
Dichlor ethyl ether		S		I	I	I		SS	SS	I			S			S	S	I	I	I
Diethylaniline																				
Diethyl carbinol																				
Diethyl carbonate																				
Diethyl phthalate																				
Diethylene glycol						I				I						S	I			
Dimethylaniline																				
Dimethyl ethyl carbinol																				
Dioxane						S				S						S	S			
Ethyl acetate (85%)		S		I	SS	S		S	SS	SC		P	SS			S	S	S	I	S
Ethyl acetoacetate						SH									S	S	S			
Ethyl alcohol		S		I	S	P		S	SS	SS		P	SS			S	S	S	I	SS
Ethyl alcohol (anhydrous)		S		I	S	P		S	SS	I		P	SS			S	I	S	I	SS
Ethyl ether		S		SS	S	S		SS	SS	I			SS			S	S	SS	I	I
Ethyl ether of diethylene glycol						P				S						SH	P			
Ethyl ether of propylene glycol																				
Ethyl lactate						SC				P		S					P			
Ethyl methyl ketone																				
Ethyl oxalate																				
Ethyl oxybutyrate																				
Ethyl sulfate																				
Ethylene chlorhydrin																				
Ethylene diacetate																				
Ethylene dichloride		S		SS	S	S		SS	SS	I			SS			S	S	SS	I	I
Ethylene glycol						I				I						P	I			
Formic acid																				
Glycerin																				
Glycol diacetate		S		I	I			SS	I	I			I			S	I	S	I	I
n-Hexanol						S				S						S	S			
Hexone						S				SC		SC					S			
2-50-W. Hi-Flash naphtha	S		I		S			S		I		I					S			
Hi-Flash naphtha (yellow)	S		I		S			S		I		I					S			
Hydrogenated naphtha	S		I		S			S		I		I					S			
Isobutyl alcohol																				
Isobutyl "Carbitol"																				
Isobutyl propionate																				
Isopropyl acetate						SC				S		P				S	S			
Isopropyl alcohol						P				S		P				S	S			
Isopropyl ether						P				I						S	S			
Kerosene																				
Lactic acid																				
Mesityl oxide																				
Methanol						P				I		I				P	I			
Methyl acetate						P				I		P				S	S			
Methyl amyl acetate						SC				I		P				S	S			
Methyl amyl alcohol						S				P		P				S	S			
Methyl amyl ketone						S	P			S	S	S		S	SS	S	S			
Methyl butyl ketone							P				S	S		S	S		S			
Methyl "Carbitol"						I				P						S	S			
Methyl "Cellosolve"						P				S						S	P			

TABLE 5.30. SOLUBILITY OF GUMS—*Continued*

Solvents	Asphalt petroleum	Gum camphor	Gum congo	Gum copal	Gum dammar	Gum dammar (dewaxed)	Gum dammar (whole)	Gum elemi	Gum guaiac	Gum kauri	Gum kauri (chips)	Gum manila	Gum mastic	Gum pontianac (nubs)	Gum rosin	Gum rosin "E"	Gum rosin ester	Gum sandarac	Gum tragacanth	Gum zanzibar
Methyl ether of propylene glycol																				
Methyl ethyl ketone						S	P			SC	S	S		S	S		S			
Methyl isobutyl ketone (hexone)						S				P		SC				S	S			
Methyl propyl ketone						S	S			P	I	SC		S	S		S			
Methyl salicylate																				
Monoethylaniline																				
Monomethylaniline																				
Naphtha	S		I		S			S		I		I					I			
Naphtha (heavy)	S		I		S			S		I		I					I			
Naphtha (nitrated)	S		I		S			S		I		I					I			
3-BX naphtha	S		I		S			S		I		I					I			
2-10M naphtha	S		I		S			S		I		I					I			
V. M. & P. naphtha	S		I		S			S		I		I					I			
Octyl acetate						SC				I		P				S	S			
Octyl alcohol						S				S		P				S	S			
Palmitic acid																				
Petroleum ether																				
Pine oil																				
Propionic acid																				
n-Propyl acetate						S				P		P					S			
n-Propyl alcohol						P				I		P					P			
Propylene dichloride						S										S	S			
Propylene glycol						I				P						S	I			
Propylene oxide						S				S						S	S			
Pyridine																				
Solvenol																				
Solvesso No. 1						S				I		I					S			
Sulfonated castor oil																				
Sulfonated caster oil 50%—Pine oil 50%																				
Toluene (nitrated)	S		I		S	S		S		I		I					S			
Toluene (industrial pure)	S		I		S			S		I		I					S			
Toluene (90/120)	S		I		S			S		I		I					S			
Trichlorethylene						S				P						S	S			
Triethylene glycol						I				I						P	I			
Troluoil						SC				I		I					P			
Turpentine																				
Xylene (5 degrees)	S		I		S	S		S		I		I					S			
Xylene (10 degrees)	S		I		S	S		S		I		I					S			
Xylene (industrial)	S		I		S	S		S		I		I					S			

TABLE 5.31. SOLUBILITY OF RESINS AND WAXES

SH	Soluble when hot	I	Insoluble	G	Gelled
VS	Very soluble	P	Partly soluble	IG	Insoluble-gelled
S	Soluble	SC	Soluble but cloudy	SSH	Slightly soluble when hot
		SS	Slightly soluble		

Solvents	Shellac	Shellac bleached	Shellac orange	Shellac stik-lac	T. N. shellac	Beeswax	Candelilla wax	Carnauba wax	Ceresin wax	Chinese or insect wax	Japan wax	Montan wax	Ozocerite wax	Paraffin wax	Spermaceti wax
Acetaldehyde		S		S	S										
Acetic acid		S		S	S										
Acetone	P	P		S	SS	SH		SH	I		SH			SH	SH
Acetophenone		SS		SS	SS										
Amyl acetate	SS	I		I	I						I				
sec-Amyl acetate			I												
Amyl acetate (mixed isomers)			I												
Amyl acetate (from fusel oil)			I												
n-Amyl alcohol	I	S		S	S						I				
sec-Amyl alcohol			P												
Amyl alcohol (mixed isomers)			S												
Amyl alcohol (from fusel oil)		S	P	S	S	S		S			S				S
Amyl chloride		I		I	I										
Amyl lactate			SC												
Benzene (nitrated pure)		IG		I	I				S	S	S	S	S		
Benzene (industrial)		IG		I	I				S	S	S	S	S		
Benzene (90% industrial)		IG		I	I				S	S	S	S	S		
Benzene (B-refined)		IG		I	I				S	S	S	S	S		
Brombenzene		IG		I	I										
Butyl acetate, 85%	I	SS		SS	SS						I				
n-Butyl acetate	I	I	I	I	I						I				
sec-Butyl acetate			I												
n-Butyl alcohol	S	S	S	S	S										
sec-Butyl alcohol		S	P	S	S										
tert-Butyl alcohol		S		S	S										
Butyl butyrate											I				
Butyl "Carbitol"	P	S		S	S										
Butyl "Cellosolve"	S	S	SC	S	S										
Butyl lactate			SC												
Butyric acid		SS		S	SS										
Carbon disulfide		I		I	I								S		S
Carbon tetrachloride		I		I	I	S	S	S			S	S		S	S
"Cellosolve"	S	S	SC	S	S						I				
"Cellosolve" acetate	S	SS	I	SS	SS						I				
Chloroform		IG		IG	IG	SH	SH	SH	P		S	S		SH	SH
Cyclochlorohexanes				I											

Table 5.31. Solubility of Resins and Waxes—*Continued*

Solvents	Shellac	Shellac bleached	Shellac orange	Shellac stik-lac	T. N. shellac	Beeswax	Candelilla wax	Carnauba wax	Ceresin wax	Chinese or insect wax	Japan wax	Montan wax	Ozocerite wax	Paraffin wax	Spermaceti wax
Cyclohexane		SS		S	SS										
Diacetone alcohol	S	S		S	S										
Dibutyl phthalate	P	I		I	I						I				
Dichlor ethyl ether	I														
Diethylaniline		I		I	I						I				
Diethyl carbinol		S		S	S										
Diethyl carbonate		I		I	I										
Diethyl phthalate		I		I	I										
Diethylene glycol	I	S		S	S										
Dimethylaniline		I		I	I										
Dimethyl ethyl carbinol		SS		SS	SS										
Dioxane	S					SH		SH				SH			
Ethyl acetate (85%)	S	SS	I	SS	SS										
Ethyl acetoacetate	SS	SS	SSH	SS	SS			SSH							SH
Ethyl alcohol	SS	S	SC	S	S	SH	SH	SH	I	SS	SH	SH	I	I	SH
Ethyl alcohol (anhydrous)	SS	S	SC	S	S	SH	SH	SH	I	SS	SH	SH	I	I	SH
Ethyl ether	SS	SS		SS	SS	S		SH		SS	SH		S	SH	S
Ethyl ether of diethylene glycol	S	S		S	S										
Ethyl ether of propylene glycol		S		S	S										
Ethyl lactate		S	SC	S	S										
Ethyl methyl ketone		SS		SS	SS										
Ethyl oxalate		SS		I	I										
Ethyl oxybutyrate		SS		SS	SS										
Ethyl sulfate		I		I	I										
Ethylene chlorhydrin		S		S	S										
Ethylene diacetate		I		I	I										
Ethylene dichloride	SS	IG		IG	IG						SS				
Ethylene glycol	P	I		I	I										
Formic acid		S		S	S										
Glycerin		I		I	I										
Glycol diacetate	I										I				
n-Hexanol	S														
Hexone			I												
2-50-W. Hi-Flash naphtha															
Hi-Flash naphtha (yellow)															
Hydrogenated naphtha									S		S				
Isobutyl alcohol		S		S	S										
Isobutyl "Carbitol"		S		S	S										
Isobutyl propionate		I		I	I										

Isopropyl acetate	S		I												
Isopropyl alcohol	S	S	S	S	S										
Isopropyl ether	I					S	S	S	S	S	S	S	S		S
Kerosene													S		
Lactic acid		SS		SS	SS										
Mesityl oxide				S											
Methanol	S	S	SC	S	S										
Methyl acetate	P		I												
Methyl amyl acetate	I		I												
Methyl amyl alcohol	P		SC												
Methyl amyl ketone	I	I				SS		SS	SS					SS	
Methyl butyl ketone		I				SS		S	SS					I	
Methyl "Carbitol"	S	S		S	S										
Methyl "Cellosolve"	S	S		S	S										
Methyl ether of propylene glycol		S		S	S										
Methyl ethyl ketone		P	I			I		I	I					I	
Methyl isobutyl ketone (hexone)	I		I												
Methyl propyl ketone		P	I			SS		I	I					I	
Methyl salicylate				I											
Monoethylaniline				SS											
Monomethylaniline		SS		SS	I										
Naphtha						I		SH	S		S	S			S
Naphtha (heavy)						I		SH	S		S	S			S
Naphtha (nitrated)						I		SH	S		S	S			S
3-BX naphtha						I		SH	S		S	S			S
2-10M naphtha						I		SH	S		S	S			S
V. M. & P. naphtha						S	S	S	S		S	S			S
Octyl acetate	I		I												
Octyl alcohol	S		I												
Palmitic acid		I		I	I										
Petroleum ether		I		I	I	I		SH			S			S	S
Pine oil						S	S	S				S			
Propionic acid		S		S	S										
n-Propyl acetate			I												
n-Propyl alcohol			P												
Propylene dichloride	I														
Propylene glycol	P	S		SS	SS										
Propylene oxide	S														
Pyridine			VS	VS	VS										
Solvenol						S	S	S				S			
Solvesso No. 1			I												
Sulfonated castor oil						S	S	S				S			
Sulfonated castor oil 50%—Pine oil 50%						S	S	S				S			
Toluene (nitrated)		IG	I	I	I				S	S	S	S	S		
Toluene (industrial pure)		IG	I	I	I				S	S	S	S	S		
Toluene (90/120)		IG	I	I	I				S	S	S	S	S		
Trichlorethylene	P					S	S	S	S	S	S	S	S		S
Triethylene glycol	I														
Troluoil			I												
Turpentine						S	S	S			S	S	S	S	S
Xylene (5 degrees)		IG	I	I	I				S	S	S	S	S		
Xylene (10 degrees)		IG	I	I	I				S	S	S	S	S		
Xylene (industrial)		IG	I	I	I				S	S	S	S	S		

TABLE 5.32. SOLUBILITY OF SYNTHETICS

1 In the presence of alcohol
2 Nitrocellulose with 35% alcohol
3 Ethyl cellulose 5% by volume
4 Ethyl cellulose 16% by volume
S Soluble
I Insoluble
P Partly soluble
SC Soluble but cloudy
SS Slightly soluble
G Gelled

Solvents	Alkyd-resins modified with—			Amberlac 94	Amberol 801	Amberol-type resin	Araclor	Beckacite 1110	Beckasol 1324	Cellulose acetate	Cellulose nitrate	Copal gum, esterified	Coumarone resin	Ethyl cellulose	Glyptal 2471	Glyptal-type resin	Lewisol 2	Neville resin	Paraplex RG-2	Rezyl 12	Santicizer B-16	Santolite M-7	Teglac Z-152	Vinyl acetate resin	Vinylite A	Durez 4032	Paranol CW	Benzyl cellulose
	Oil	Phenol	Natural resins																									
Acetone						S				S	S		S	S		S		S						S	S			P
Amyl acetate										I	S		S	S_3				S						S				S
sec-Amyl acetate				S	S		S	S	S		S				P		P		S	P	S	S	S			S	S	
Amyl acetate (mixed isomers)				S	S		S	S	S		S				S		S		S	S	S	S	S			S	S	
Amyl acetate (from fusel oil)				S	S		S	S	S		S				P		S		S	S	S	S	S			S	S	
n-Amyl alcohol										I	I		P	S_3										P				I
sec-Amyl alcohol				P	I		P	P	S		I				P		P		S	I	S	P	P			P	P	
Amyl alcohol (mixed isomers)				P	P		P	P	S		I				P		P		S	I	S	P	I			S	P	
Amyl alcohol (from fusel oil)				P	I		P	I	S		I				P		P		S	I	S	P	I			S	P	
Amyl formate										I	S		S															
Amyl lactate				S	S		S	S	S	I	S		S		S		S		S	S	S	S	S			S	S	
Amyl propionate										I	S		S											S				
Amyl stearate																		S										
Benzene (nitrated pure)	S	S	S							I	I		S	S_3		I		S						P				S
Benzene (90% industrial)	S	S	S							I	I																	
Benzene (B-refined)	S	S	S							I	I																	
Benzyl acetate											S		S															
Benzyl alcohol										S			S	S		S												
Benzyl formate										S	S		S			S												
Butyl acetate, 85%										S	S																	
n-Butyl acetate				S	S		S	S	S	I	S		S	S_3	S		S	S	S	S	S	S	S	S	S	S	S	S
sec-Butyl acetate				S	S		S	S	S	I	S		S	S	P		S		S	P	S	S	S			S	S	
n-Butyl alcohol				S	P		P	P	S	I	I		P	S_3	P		P		S	I	S	P	I	P	P	S	S	I
sec-Butyl alcohol				P	I		P	I	S	I	I				P		P		S	I	S	P	I			P	P	
Butyl butyrate										I	SS		S	S														
Butyl "Carbitol"										I															S			
Butyl "Cellosolve"				S	S		S	S	S	I	S		S	S_3	S		S	S	S	S	S	S	S		P	S	S	P
Butyl formate										I	S		S															
Butyl lactate				S	S		S	S	S	I	S		S	S_3	S	S	S		S	S	SC	S	S	S		S	S	P
Butyl oxalate																		S										
Butyl propionate										I	S		S			I		S						S				
Carbon disulfide													S					S										
Carbon tetrachloride										I	S_2		S	S_3		I		S						P				G
"Cellosolve"				S	S		S	S	S	G	S		S	S_3	S		S	S	S	S	S	S	S		S	S	S	S
"Cellosolve" acetate				S	S		S	S	S	G	S			S_3	S		S		S	S	S	S	S		S	S	S	S

Chlorbenzene										I	I		S	S				S						S				
Chlorinated naphthalene													S					S										
Chloroform										I			S	S_3				S										S
Coal tar oils													S															
Cyclohexanone										P	S_2		S	S_3		S		S						S				S
Cyclohexanyl acetate										S	S			S										S				
Cyclohexane														S_3														
Cyclohexanol (Hexalin)										I	I		S	PS_3		S		S						I				P
Diacetone alcohol										S	S		S	I		S		S						S				
Diamyl phthalate																		S										
Dibutyl phthalate										P			S					S							S			
Dichlor ethyl ether										S_1	I		S	PS_3		S								I	S			
Dichlorethane													S	S		S								S				
Dichlorhydrin											S		S	S		S												
Diethyl carbonate										I	S		I			I								I				
Diethylene glycol										I	S		I					I							I			
Dioxane										S	S_2		S	S_3		S		S						S	S			S
Dipropyl ketone										S	S		S	S		S								S				
Ethanolamine																		I										
Ethyl acetate (pure 85%)				S	S		S	S	S	SS	S		S	S_3	S	I	S	S	S	S	S	S	S	S	S	S	S	S
Ethyl alcohol										I	I			S_3		I		I						P	S			I
Ethyl alcohol (anhydrous)				P	I		I	I	SC		P				P		I		S	I	S	S	I			S	I	
Ethyl benzoate										S	S		S	S		S												
Ethyl butyrate										I	S		S	S		I												
Ethyl "Carbitol"										I															P			
Ethyl ether										I	S	I	I	S_4				S							I			I
Ethyl lactate				S	P		S	S	S	S	S		S	S_3	S	S	S	S	S	S	S	S	S	S		S	S	P
Ethylene dichloride										S_1	S_1			S_3											S			S
Ethylene glycol										I								I							I			
Furfural										S	S		S	S		S												
Furfuryl acetate											S		S															
Furfuralcohol											S		S															
Gasoline																		S										
Glycerin																		I										
Glycol diacetate										S	S		I	S_3														P
Hexyl acetate										I	S		S					S						S				
2-50-W. Hi-Flash naphtha	S	S	S							I	I		S	PS_3				S										
Hi-Flash naphtha (yellow)	S	S	S							I	I		S	PS_3				S										
Hydrogenated naphtha	S	S	S																									
Isobutyl acetate										I	S		S	S				S						S				
Isobutyl propionate										I	S																	
Isopropyl acetate				S	S		S	S	S	I	S		S	S_3	S		S	S	S	S	S	S	S	S	S	S	S	P
Isopropyl alcohol				S	I		I	I	SC	I	I			S_3	SC		I		S	I	S	I	I	I	S	S	I	
Isopropyl ether										I															I			
Methanol				P	I		I	I	SC	I	P			S_3	P		S	I	I	I	S	S	I	S	S	S	I	
Methyl acetate				S	S		S	S	S	S	S		I	S_3	S	S	S		S	S	S	S	S	S	S	S	S	
Methyl amyl acetate				S	S		S	S	P	I	S				S		P		S	I	S	P	S		S	S	S	
Methyl amyl alcohol				S	P		P	P	S	I	I				P		P		S	I	S	P	I		S	S	S	
Methyl amyl ketone						S				I	S		S	S		S								S	S			
Methyl butyl ketone						S				I	S		S	S		S								S				
Methyl "Carbitol"										S															S			
Methyl "Cellosolve"										S	S_2			S_3				I							S			P
Methyl "Cellosolve" acetate										S	S_2			S_3														S
Methyl cyclohexanol										I	I		S	S		S								S				

TABLE 5.32. SOLUBILITY OF SYNTHETICS—*Continued*

Solvents	Alkyd-resins modified with—			Amberlac 94	Amberol 801	Amberol-type resin	Araclor	Beckacite 1110	Beckasol 1324	Cellulose acetate	Cellulose nitrate	Copal gum, esterified	Coumarone resin	Ethyl cellulose	Glyptal 2471	Glyptal-type resin	Lewisol 2	Neville resin	Paraplex RG-2	Rezyl 12	Santicizer B-16	Santolite M-7	Teglac Z-152	Vinyl acetate resin	Vinylite A	Durez 4032	Paranol CW	Benzyl cellulose
	Oil	Phenol	Natural resins																									
Methyl cyclohexanone										S	S		S	S		S								S				
Methyl cyclohexanyl acetate										P	S			S														
Methyl ethyl ketone				S	S	S	S	S	S	S_1	S		S	S	S	S	S		S	S	S	S	S	S		S	S	S
Methyl isobutyl ketone (hexone)				S	S		S	S	S	I	S				S		S		S	S	S	S	S		S	S	S	
Methyl isopropyl ketone				S	S		S	S	S		S				S		S		S	S	S	S	S			S	S	
Methyl propyl ketone				S	S	S	S	S	S	I	S		S	S	S	S	S		S	S	S	S	S	S		S	S	
Mineral spirits																		S										
Naphtha	S	S	S							I	I							S										
Naphtha (heavy)	S	S	S							I	I																	
Naphtha (nitrated)	S	S	S							I	I																	
3-BX naphtha	S	S	S							I	I																	
2-10M naphtha	S	S	S							I	I																	
V. M. & P. naphtha	S	S	S							I	I			I														I
Octyl acetate				S	S		S	S	S	I	S				S		P		S	I	S	I	S		P	S	S	
Octyl alcohol				P	P		P	P	S	I	I				P		P		S	I	S	I	P		P	S	S	
Petroleum thinners																		S										
Pine oil													S					S										
n-Propyl acetate				S	S		S	S	S	S	S		S	S_3	S		S	S	S	S	S	S	P	S		S	S	S
n-Propyl alcohol				S	I		P	I	S	I	S_2			PS_3	P		P		S	I	S	P	I	I		S	I	I
Propylene glycol										I															I			
Pyridine																		S										
Rosin oil													S					S										
Solvent naphtha																		S										
Solvesso No. 1				S	S		S	S	S		I				S		S	S	I	I	S	I	S			I	S	
Terpineol													S					S										
Tetrahydrofurfuryl alcoho											S		S											S				
Tetralin										I	I		S	S_4														
Toluene (nitrated)	S	S	S	S	S		S	S	S	I	I		S	S_3	S	I	S	S	S	S	S	S	S	P		S	S	P
Toluene (industrial pure)	S	S	S							I	I																	
Toluene (90/120)	S	S	S							I	I																	
Trichlorethylene										I	I		S	S_3										S	S			S
Tricresyl phosphate													S					S										
Triethylene glycol										I															S			
Triphenyl phosphate													S					S										
Troluoil				I	I		S	I	I		I				I		I		I	I	S	I	I			I	S	
Turpentine											S_2		S					S										I
Xylene (5 degrees)	S	S	S	S	S		S	S	S	I	I		S	S_3	S	I	S	S	S	S	S	S	S	I		S	S	
Xylene (10 degrees)	S	S	S							I	I																	
Xylene (industrial)	S	S	S							I	I																	

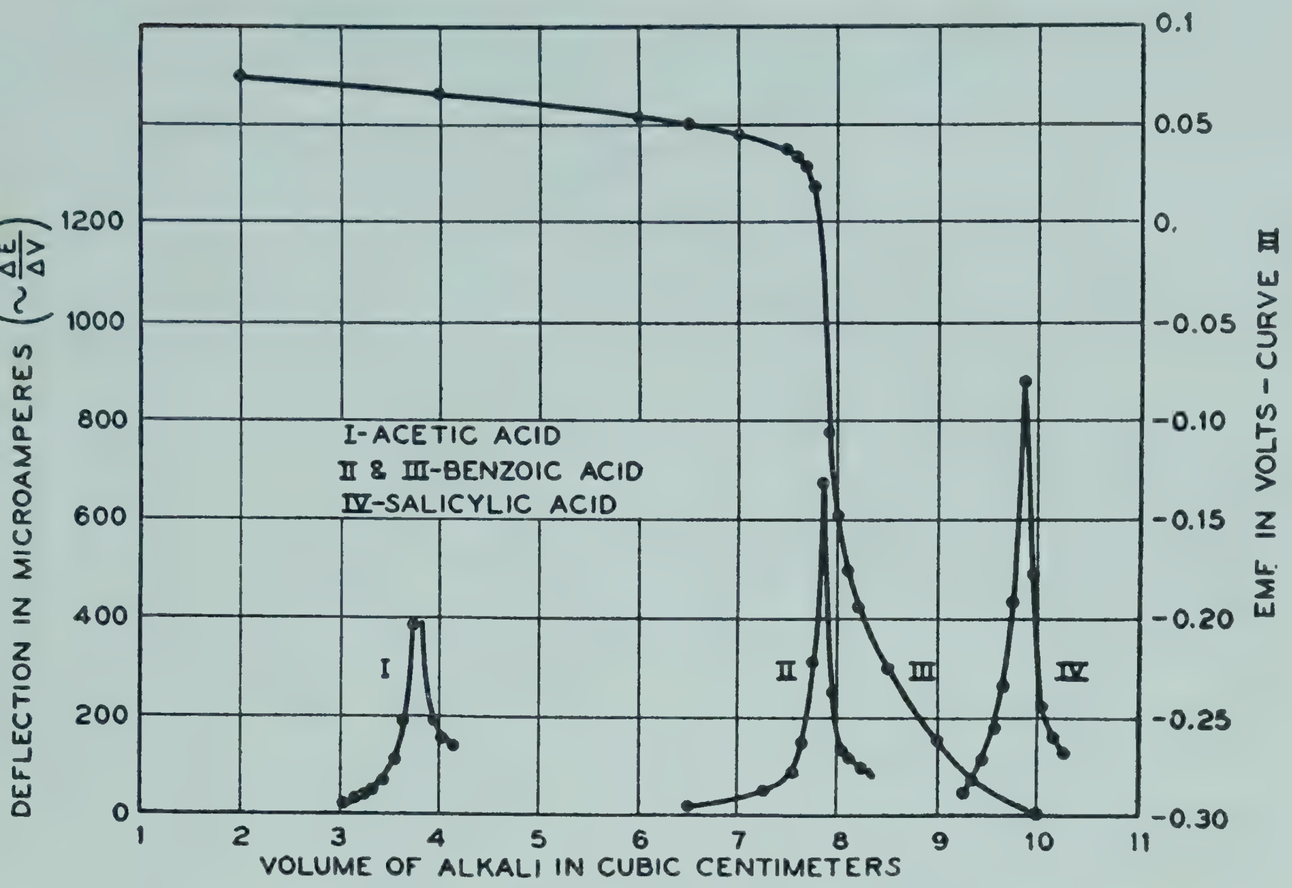


Figure 5.11. Titrations in Acetone-Butyl Alcohol[40]

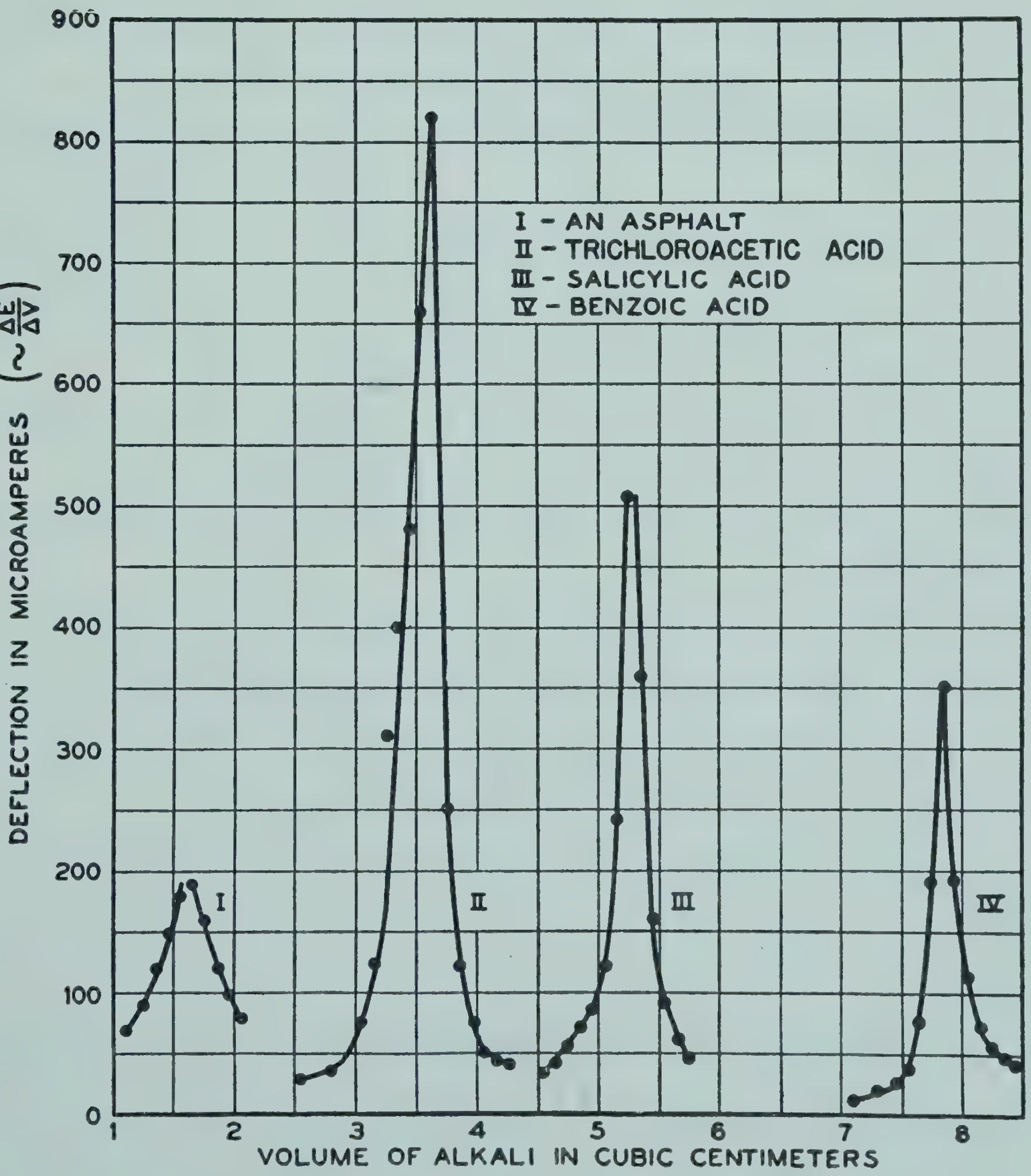


Figure 5.12. Titrations in Anisol-Butyl Alcohol.[40]

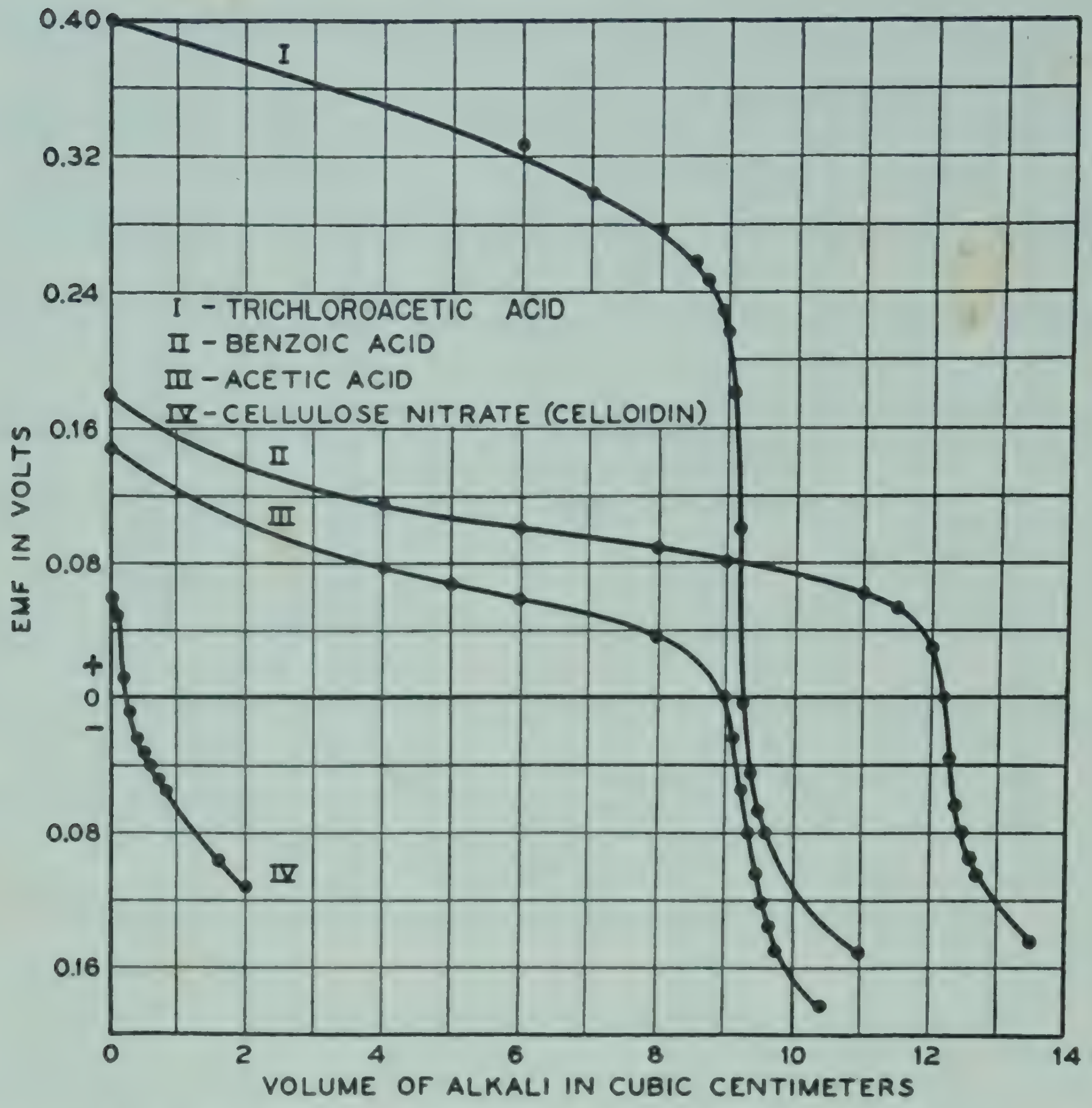


Figure 5.13. Titrations in Ethylene Glycol Monomethyl Ether.[40]

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Chapter 6

Safe Handling of Solvents

Flammability

In the spring of 1949 a serious accident occurred in the Holland Tunnel connecting New York City with New Jersey. A truck carrying a number of drums of carbon disulfide caught fire when about half way through the tunnel, and the heat was sufficient to cause an explosion which wrecked a large section of the tube and endangered the lives of hundreds of motorists. The materials which are allowed to be transported through the tunnel are closely regulated by the Port of New York Authority, and it was established that carbon disulfide is an illegal cargo item.

It was extremely fortunate that no lives were lost as a result of this avoidable disaster; as it was, many autoists and rescuers were overcome by toxic fumes, and only intelligent handling of the situation by fire and police authorities prevented fatalities.

This is a dramatic instance of the consequences of improper handling of solvents. In this case several factors combined to make them particularly bad (1) the extreme sensitivity of carbon disulfide to heat (its vapor ignites spontaneously at about 212° F); (2) the fact that it gives off poisonous fumes; and (3) the circumstances of the explosion, which occurred in a partially enclosed area where quick dissipation of the fumes was impossible. Carbon disulfide is one of the most dangerous of all commercial solvents, and its storage, transportation and conditions of use should be strictly supervised. For example, it should not be used around hot metal, electric lamps, or in any location where sparks are likely to occur.

The striking news value of this accident gave it nationwide attention for several days; but thousands of others occur each year from improper solvent handling, many of them causing permanent injury or death, and all costing a tremendous amount of money. In 1943 there was a record loss (about $14,000,000) from fires due to this cause.[1] The number of individual fires runs from 20 to 25 thousand a year, most of them in the paint, varnish and dry-cleaning industry. It is therefore of the utmost importance to establish and enforce safety codes in all manufacturing operations where solvents are used.

A sizable literature has grown up on the subject of safe handling of solvents. The Safety Research Institute (New York) and the National

Safety Council (Washington) have consistently advocated better understanding of the subject by all who make and use dangerously flammable materials. In addition to articles listed in the bibliographies of this chapter, reference should be made to the excellent and detailed bulletins prepared by the Manufacturing Chemists' Association (Washington, D. C.), which give complete hazard and safety data for a number of commonly used solvents. The National Fire Protection Association (Boston, Mass.) has advocated a number of important regulations governing solvent handling.[1]

"1. All flames and smoking must be eliminated.

"2. All sources of sparks must be removed; rubber soled shoes and nonferrous tools should be employed.

"3. All equipment for handling flammable solvents should be electrically grounded.

"4. Main supplies of solvents should be stored in a fireproof storage building. Solvent cans should be of the safety type.

"5. In spray booths, all parts of the system should be constructed of fire-resistant material, and all surfaces should be smooth to facilitate routine cleaning.

"6. All electric lights in spray booths or near solvent-using processes should be of the vapor-proof type; electric wiring should be enclosed and should follow the requirements of the National Electric Safety Code.

"7. Fire extinguishers, of types approved for thc class of hazard concerned, should be provided as protcction against incipient fires."

The Bureau of Explosives of the U. S. Dept. of Mines (30 Vesey St., New York) issues periodic bulletins governing the labels and other transportation regulations for shipping flammable and explosive materials.

Many of the most useful properties of solvents are a result of volatility —the tendency of molecules or molecular aggregates to leave the surface of the liquid. The rate of vaporization depends on many factors: the chemical nature of the solvent—that is, whether its molecules are simple or complex—the temperature, the barometric pressure, and the rate at which air passes over its surface. As a result of vaporization, especially in confined areas or in still air, a high concentration of molecules of the solvent develops in the air immediately above it. It is this vapor-air mixture which is actually flammable, rather than the liquid itself. Thus volatility, useful as it is, carries with it the penalty of fire hazard. Fans and other ventilating devices are among the most essential means of reducing flammability hazards in a plant where solvent vapors are likely to accumulate, as they prevent development of high concentrations of fumes. The vapors of most of the common organic solvents are very flammable, although those of chlorinated hydrocarbons are somewhat less so. Underwriters' Laboratories have rated organic solvents in respect to flammability by a scale on which carbon tetrachloride is zero and carbon disulfide 100.[1]

Flash Point

Three properties having to do with flammability are generally recognized They are somewhat similar, but by no means identical, and should not be confused. The first of these is the *flash point*, by which is meant "the lowest temperature at which enough vapors are given off to form a flammable mixture of vapors and air immediately above the liquid surface."[2] This implies the presence of a spark or open flame. The flash points of various solvents differ widely. The barometric pressure affects them, just as it does boiling point. It is essential to realize that flash point varies with pressure and that it is quite possible to have an ignitable or explosive mixture far below the stated flash-point value at pressures less than 760 mm. Hg, that is, under partial vacuum, since obviously the lower the pressure the greater will be the tendency of molecules to leave the liquid surface. Flash point is also affected by temperature and by molecular structure, solvents having simpler molecules being more easily ignited.

There are several ways of determining flash points, but that most often used is the so called "open cup" method. All techniques are not equally reliable, and in quoting flash point values it is essential to mention the method by which it was determined; otherwise the values can be misleading. It is interesting to note that the flash point of gasoline is −50° F; for many other solvents, especially ethers, it lies well below 0° F. Extra precautions should be observed in storing, transporting or using any of these liquids—for example, the practice of carrying a contact chain on gasoline trucks to ground any possible sparks resulting from static electricity due to friction of the liquid on the tank walls. Solvents having exceptionally low flash point values, and therefore highly susceptible to ignition at low temperatures, are as follows:

Acetaldehyde	−17° F
Carbon disulfide	−22
Diethyl ether	−20
Dimethyl ether	−42
Ethyl chloride	−53
Gasoline	−50
Isobutyraldehyde	−40
Methyl ethyl ether	−35
Petroleum ether	−50

A list of the flash points of the most common solvents will be found in Table 6.1.

Determinations of the flash points of various mixtures of solvents have been made, some of which are given in Table 6.2. If a given solvent is mixed with water its flash point occurs at progressively higher temperatures, i.e., the solvent-water mixture is safer than the pure solvent under identical conditions. This is illustrated in the case of ethyl alcohol in Table 6.3. When non-flammable liquids, such as water or carbon tetrachloride are added to a solvent with the idea of rendering the mixture safe from the standpoint of ignitability, evaporation will occur, and the mixture may not remain constant in composition, as some of the constituents may evaporate faster than the others. If molecular aggregates are so formed as to give a higher flash point or to make the mixture non-flammable, its composition will remain constant during evaporation. When no molecular aggregates are formed, it is entirely possible for a non-flammable mixture to become flammable by evaporation loss of the protecting component.

Fire Point

The *fire point* of a solvent has been defined[2] as "the lowest temperature at which a liquid will give off enough vapor to continue to burn when once ignited." The fire point is less often given in the literature, but it is usually a little higher than the flash point.

Auto-ignition Point

That temperature at which a mixture of a solvent vapor and air will ignite without the aid of a spark or flame is known as the auto-ignition point of the solvent.[2] This tendency of certain liquids to catch fire spontaneously can result in serious fires or explosions if proper precautions are not taken. Such liquids give off heat when they vaporize, and if they are in a confined space where the heat builds up faster than it can be dissipated, spontaneous combustion will occur. As might be expected, the auto-ignition temperature is very much higher than the flash point; for example in the case of carbon disulfide, the former is 212° F and the latter −22° F. A list of the ignition points of typical solvents is given in Table 6.1, and ignitable concentrations of mixed solvents in Table 6.4.

Explosive Range

Closely related to the three flammability properties discussed above is the range of concentrations of vapor in air which will propagate a flame, or which will explode under confined conditions.[2] In some cases the lowest explosive concentration is no more than 1% (carbon disulfide), and on the high side it may reach over 50% (acetaldehyde). Values for these ranges are given in Table 6.1. There is no explosion hazard if the concentration of flammable vapor exceeds that given in the column headed "Upper Limit," as in this case the mixture is actually so concentrated (or "rich") that it

(*Text continued on page 208*)

TABLE 6.1. PROPERTIES OF FLAMMABLE LIQUIDS, GASES AND SOLIDS

NAME	SYNONYMS	Flash Point °F		Explosive Limits % by Vol. in Air		Autoignition Temp. °F.	Susceptibility to Spontaneous Heating	Specific Gravity (Water = 1.00)	Vapor Density (Air = 1.00)
		Closed Cup	Open Cup	Lower	Upper				
Acetal	Acetaldehydediethyl-acetal	-5	....	1.65	...	446	..	0.821	4.08
Acetaldehyde		-17	....	4.0	57.0	365	No	0.783	1.52
Acetanilide	Antifebrin	345	345	...	...	..	..	1.21	4.65
Acetic Acid (Glacial)		104	110	4.0	...	1050	No	1.05	2.07
Acetic Anhydride		121	130	...	...	752	No	1.08	3.52
Acetone	Dimethyl Ketone	0	15	2.15	13.0	1118	No	0.792	2.00
Acetophenone	Phenyl Methyl Ketone	221	....	...	...	..	No	1.03	4.14
p-Acetotoluide	Tolylacetamide	335	355	...	...	....	..	1.212	5.14
Acetyl Chloride		40	....	...	...	....	No	1.105	2.70
Acetylene		gas	....	2.5	80	635	No	.....	0.91
Acetylene Tetrabromide	Tetrabromoethane	non-flammable		...	...	..	No	2.97	....
Acetylene Tetrachloride	Tetrachloroethane	non-flammable		...	...	..	No	1.58	5.73
Acrylonitrile		....	32	3.05	...	898	..	0.8004	1.83
Adipic Acid		385	....	...	...	..	..	.....	5.04
Aldol		181	....	...	...	..	No	1.11	3.04
Allyl Alcohol		70	75	3.0	...	713	No	0.854	2.00
Allylene		gas	....	1.74	...	....	..	.....	0.66
Aluminum (Powder)*		....	....	...	...	....	No	.....	....
Ammonia (Anhydrous)		gas	....	16.0	27.0	1436	No	.....	0.597
Amyl Acetate-n		76	80	1.1	...	714	No	0.879	4.49
Amyl Acetate-iso		92	100	...	...	715	No	0.876	4.49
Amyl Alcohol-n	Fusel Oil	91	120	1.2	...	621	No	0.817	3.04
Amyl Alcohol- prim. iso	Butyl Carbinol	109	115	...	...	667	No	0.813	3.04
Amyl Alcohol- sec. n		94	....	...	...	650–725	No	0.810	3.04
Amyl Alcohol- sec. iso	Methyl iso-Propyl Carbinol	103	....	...	...	....	No	0.819	3.04
Amyl Chloride		....	....	1.4	...	....	No	0.878	3.67
Amylene-n		....	....	1.6	...	....	No	0.666	2.42
Amyl Naphthalene		....	255	...	...	....	..	0.973	6.86
Amyl Salicylate		270	....	...	...	....	..	1.065	7.17
Aniline	Amino Benzene	168	....	...	...	1418	No	1.022	3.22
Aniline Hydrochloride		....	380	...	...	....	No	1.22	4.46
Anthracene		250	385	0.63	...	881 in O_2	No	1.25	1.15
Anthraquinone		365	485	...	...	....	No	1.438	7.16
Asphalt (Typical)		400+	535+	...	...	905	No	0.95–1.1	....
Benzaldehyde	Artificial Almond Oil	148	165	...	...	....	No	1.05	3.66
Benzene	Benzol	12	....	1.4	8	1076	No	0.88	2.77
Benzoic Acid		250	....	...	...	....	No	1.266	4.21
Benzoyl Chloride		215	....	...	...	....	..	1.212	4.88
Benzyl Acetate		216	....	...	...	862	No	1.06	5.17
Benzyl Alcohol	Phenyl Carbinol	213	220	...	...	817	No	1.04	3.72

TABLE 6.1. PROPERTIES OF FLAMMABLE LIQUIDS, GASES AND SOLID—*Continued*

NAME	SYNONYMS	Flash Point °F		Explosive Limits % by Vol. in Air		Autoignition Temp. °F.	Susceptibility to Spontaneous Heating	Specific Gravity (Water = 1.00)	Vapor Density (Air = 1.00)
		Closed Cup	Open Cup	Lower	Upper				
Benzyl Benzoate		298	....	...	...	....	No	1.114	7.31
Benzyl Cellosolve		....	265	...	...	....	No	1.07	....
Benzyl Chloride		140	....	1.1	...	....	No	1.103	4.36
Borneol		150	....	...	...	....	No	1.01	5.31
Bromobenzene	Phenyl Bromide	149	....	...	...	....	No	1.497	5.41
Bronze Dust (Aluminum Free)		No Hazard		...	...	....	No	.....	....
Butadiene-1, 3	Erythrene	Gas	....	2.0	11.5	....	..	0.621	1.87
Butane-n		–76	gas	1.6	8.5	806	No	.....	2.046
Butyl Acetate-n		72	90	1.7	15	790	No	0.88	4.00
Butyl Acetate-iso		64	....	...	...	....	No	0.871	4.00
Butyl Alcohol-n		84	110	1.7	...	693	No	0.806	2.55
Butyl Alcohol-iso		82	....	1.68	...	825	No	0.805	2.55
Butyl Alcohol-ter.		52	....	...	...	901	No	0.786	2.55
Butyl Benzene-sec.		126	....	...	...	....	No	0.86	4.62
Butyl Carbitol		172	200	...	...	442	No	0.955	5.58
Butyl Carbitol Acetate		....	240	...	...	....	No	0.987	....
Butyl Cellosolve		141	165	...	...	472	No	0.902	4.07
Butyl Chloride-n	I-chloro-butane	....	20	1.85	10.1	860	..	0.887	3.20
Butyl Decalin		500	....	...	...	....	..	.....	....
Butyl Decalin-ter.		640	....	...	...	....	..	.....	....
Butylene-n		gas	....	1.7	9.0	....	No	.....	0.668
Butylene Chloride		....	....	2.25	9.25	....	..	0.926	3.13
Butylene Glycol		104	....	...	...	....	No	1.019	3.10
Butyl Formate-n		64	....	...	...	....	No	0.911	3.52
Butyl Lactate		160	....	...	...	....	No	0.968	5.04
Butyl Naphthalene		680	....	...	...	....	..	.....	...
Butyl Phthallyl Butyl Glycollate		385	390	...	...	....	No	>1	....
Butyl Propionate-n		90	110	...	...	800	No	0.875	5.00
Butyl Ricinoleate		230	....	...	...	....	..	0.906	....
Butyl Stearate-n		320	385	...	...	....	..	0.855	....
Butyl Tetralin-ter.		680	....	...	...	....	..	.....	....
Butyraldehyde		20	....	...	...	....	No	0.817	2.48
Butyraldoxime	Butanal Oxime	136	....	...	...	....	..	0.923	3.01
Butyric Acid-n		170	....	...	...	....	No	0.960	3.04
Butyric Anhydride-n		190	....	...	...	....	..	0.978	5.38
Butyrone		120	....	...	...	....	No	0.815	3.93
Camphor		150	200	...	...	871	No	0.999	5.24
Camphor Oil (Light)		117	125	...	...	....	No	0.88	....
Carbitol		201	215	...	...	....	No	0.99	4.62
Carbitol Acetate		225	230	...	...	....	No	1.013	6.07
Carbon Disulfide		–22	....	1.0	50	257	No	1.256	2.64
Carbon Monoxide		gas	....	12.5	74.2	1204	No	.....	0.967
Carbonyl Sulfide	Carbon Oxysulfide	....	....	11.9	28.5	....	..	1.24	2.10
Carnauba Wax		540	595	...	...	....	..	.....	....
Castor Oil		445	545	...	...	840	Yes	0.96	....
Cellosolve	Ethyl Cellosolve	104	120	2.6	15.7	460	No	0.931	3.10

TABLE 6.1. PROPERTIES OF FLAMMABLE LIQUIDS, GASES AND SOLIDS—*Continued*

NAME	SYNONYMS	Flash Point °F		Explosive Limits % by Vol. in Air		Autoignition Temp. °F.	Susceptibilitp to Spontaneous Heating	Specific Gravity (Water = 1.00)	Vapo Densi (Air = 1.00)
		Closed Cup	Open Cup	Lower	Upper				
Cellosolve Acetate		124	135	1.71	...	715	No	0.975	4.72
Charcoal	Carbon	...	...	...	...	....	Yes	3.51	....
Chlorobenzene	Phenyl Chloride	90	....	...	...	....	No	1.11	3.88
Chloroethyl Acetate		129	....	...	...	....	..	1.178	4.21
Chloroform	Trichloromethane	non-flammable		...	...	....	No	1.489	4.13
Chloronitroethane-1, 1		....	133	...	...	....	..	1.258	3.77
Chloronitropropane-1, 1		....	144	...	...	....	..	1.209	4.26
Chloronitropropane-2, 2		....	135	...	...	....	..	1.193	4.26
Coal Tar Pitch		405	490	...	...	....	..	.....	....
Cocoanut Oil		420	510	...	...	....	Yes	0.91	....
Corn Oil		490	....	...	...	....	Yes	0.92	....
Cottonseed Oil		590	....	...	...	650	Yes	0.925	...
Creosote Oil		165	185	...	...	637	No	>1	...
o-Cresol	o-Methyl Phenol	178	....	...	...	....	No	1.05	3.72
p-Cresol	Cresylic Acid	187	....	...	...	....	No	1.04	3.72
Crotonaldehyde		55	....	2.95	15.5	....	No	0.853	2.41
Crotonylene		....	....	1.37	...	....	..	.....	...
Cyanamide		285	405	...	...	....	..	1.073	1.4
Cyclohexane		1	....	1.31	8.35	....	No	0.779	2.9
Cyclohexanol	Hexalin	154	....	...	...	....	No	0.962	3.4
Cyclohexanone		147	....	...	...	....	No	0.947	3.3
Cyclohexanone delta		93	....	...	...	....	No	.....	3.31
Cyclohexyl Acetate	Hexalin Acetate	136	....	...	...	....	No	.....	4.9
Cyclohexylamine		....	90	...	...	....	..	0.865	3.4
Cyclopropane	Trimethylene	gas	....	2.41	10.3	....	No	.....	1.4
p-Cymene		117	145	...	...	921	No	0.86	4.6
Decahydronaphthalene	Decalin	136	....	...	...	504	No	0.895	4.7
Decane-n		115	....	0.67	2.6	>500	No	0.730	4.9
Denatured Alcohol—95%		60	....	...	...	....	No	0.82	1.6
DiacetoneAlcohol(comm'l)		48	55	...	...	....	No	0.931	4.0
Diamy Phenoxy Ethanol		....	300	...	...	....	..	0.959	9.6
Diamyl Phthalate		245	340	...	...	....	..	.....	...
Dianisidine		403	....	...	...	....	..	.....	...
Dibenzyl Ether		275	....	...	...	....	No	1.036	6.8
Dibutyl Ether-n		77	....	...	...	....	No	0.769	4.4

TABLE 6.1. PROPERTIES OF FLAMMABLE LIQUIDS, GASES AND SOLIDS—*Continued*

NAME	SYNONYMS	Flash Point °F		Explosive Limits % by Vol. in Air		Autoignition Temp. °F.	Susceptibility to Spontaneous Heating	Specific Gravity (Water = 1.00)	Vapor Density (Air = 1.00)
		Closed Cup	Open Cup	Lower	Upper				
Dibutyl Oxalate-n		**220**	....	...	...	....	**No**	**1.01**	....
Dibutyl Phthalate-n		**315**	**335**	...	...	....	**No**	**1.045**	**9.58**
Dibutyl Phthalate-iso		**322**	....	...	...	....	**No**	.....	**9.58**
Dibutyl Sebacate		....	**353**	...	...	....	..	**.936**	....
Dibutyl Tartrate-n		**195**	**230**	...	...	....	**No**	**1.098**	**9.03**
o-Dichlorobenzene		**151**	**165**	...	...	....	**No**	**1.325**	**5.07**
p-Dichlorobenzene		**150**	**165**	...	...	....	**No**	**1.458**	**5.07**
Dichlorodifluoromethane	**Freon, F-12**	**non-flammable**		...	...	....	**No**	.....	....
Dichloro Ethylene 1, 1	**Dichloro Ethene 1, 1**	**57**	....	**5.6**	**13**	**856**	**No**	**1.250**	**3.35**
Dichoro Ethylene 1, 2	**Acetylene Dichloride**	**43**	....	**9.7**	**12.8**	....	**No**	**1.282**	**3.35**
Dichloroethyl Ether-sym.		**131**	**185**	...	...	**696**	**No**	**1.22**	**4.93**
Dichloroisopropyl Ether		....	**185**	...	...	....	**No**	**1.113**	....
1, 1 Dichloro, 1 Nitro Ethane		....	**168**	...	...	....	..	**1.405**	**4.97**
1, 1 Dichloro, 1 Nitro Propane		....	**151**	...	...	....	..	**1.314**	**5.45**
Dichlorotetrafluoroethane	**F-114**	**non-flammable**		...	...	....	**No**	.....	....
Dicyclohexylamine		....	**>210**	...	...	....	..	**0.910**	**6.27**
Diethanolamine		....	**280**	...	...	**1224**	**No**	**1.097**	**3.65**
Diethylamine		**<0**	**<0**	...	...	....	..	**0.710**	**2.53**
Diethylaminoethanol		....	**140**	...	...	....	**No**	**0.885**	....
Diethyl Carbitol		....	**180**	...	...	....	**No**	**0.908**	....
Diethyl Carbonate		**77**	....	...	...	....	**No**	**0.977**	**4.07**
Diethyl Cellosolve		....	**95**	...	...	....	**No**	**0.842**	....
Diethyl Diphenyl Urea		**302**	....	...	...	....	..	.....	....
Diethylene Glycol		**255**	**290**	...	...	**444**	**No**	**1.119**	**3.66**
Diethylene Oxide	**Dioxan**	**65**	....	**1.97**	**22.2**	....	..	**1.035**	**3.03**
Diethylene Triamine		....	**215**	...	...	....	..	**0.954**	**3.48**
Diethyl Ether	**Ether**	**–20**	....	**1.7**	**48.0**	**366**	**No**	**0.71**	**2.55**
Diethyl Glycophthalate		**343**	....	...	...	....	..	......	.....
p-Diethyl Phthalate		**243**	**305**	...	...	....	..	**1.110**	**7.66**
Diethyl Selenide		....	....	**2.5**	...	....	**No**	**1.23**	**4.73**
Diethyl Sulfate		**220**	....	...	...	....	**No**	**1.184**	**5.31**
Diglycol Chlorohydrin		....	**225**	...	...	....	**No**	**1.172**	....
Dimethoxy Tetraglycol		....	**285**	...	...	....	**No**	**1.013**	....
Dimethyl Aniline		**145**	**170**	...	...	**700**	**No**	**0.956**	**4.17**
p-Dimethyl Cyclohexane	**Hexahydroxylol**	**52**	....	...	...	....	**No**	**0.77**	**3.86**
Dimethyl Ether	**Methyl Ether**	**–42**	....	...	...	....	**No**	.....	**1.617**
Dimethyl Glycophthalate		**369**	....	...	...	....	**No**	.....	**9.72**
o-Dimethyl Phthalate		**295**	**325**	...	...	....	**No**	**1.189**	**6.69**
Dimethyl Sulfate	**Methyl Sulfate**	**182**	**240**	...	...	....	**No**	**1.332**	**4.35**
Dinitro Aniline-2, 4		**435**	**510**	...	...	....	..	**1.615**	**6.31**
Dinitro Benzene		302	....	...	...	....	..	1.59	5.79
Dinitro Chlorobenzene		382	405	...	...	....	..	1.68	6.98
Dinitro Toluene-2, 4		...	....	...	...	....	No	1.52	6.27
Diphenyl		235	255	...	...	....	No	1.041	5.31
Diphenylamine		307	..	..	...	...	No	1.16	5.82
Diphenyl Methane	Ditane	266	...	...	...	....	No	1.006	5.79
Diphenyl Oxide	Diphenyl Ether	239	....	...	...	....	No	1.073	5.86
Dipropylene Glycol		...	280	...	..	....	No	1.040	....
Divinyl Ether	Vinyl Ether	<-22		1.7	27.0	680	No	0.774	

TABLE 6.1. PROPERTIES OF FLAMMABLE LIQUIDS, GASES AND SOLIDS—*Continued*

NAME	SYNONYMS	Flash Point °F		Explosive Limits % by Vol. in Air		Autoignition Temp. °F.	Susceptibility to Spontaneous Heating	Specific Gravity (Water = 1.00)	Vapor Densit (Air = 1.00)
		Closed Cup	Open Cup	Lower	Upper				
Dodecane	Dihexyl	165	....	0.6	...	....	No	0.750	5.86
Ester Gum		375	555	...	...	....	No	.....	....
Ethane		gas	....	3.12	15.0	950	No	.....	1.049
Ethanolamine		....	200	...	...	....	No	1.02	2.10
Ethyl Acetanilide		126	....	...	...	....	..	0.942	4.72
Ethyl Acetate	Acetic Ether	24	30	2.18	11.5	907	No	0.899	3.04
Ethyl Acetoacetate	Acetoacetic Ester	184	....	...	...	....	No	1.03	4.48
Ethyl Alcohol	Ethanol	55	....	3.28	19	799	No	0.79	1.59
Ethyl Benzene	Phenyl Ethane	59	75	...	...	....	No	0.868	3.66
Ethyl Bromide	Bromoethane	....	....	6.75	11.25	952	No	1.430	3.76
Ethyl Butyl Carbonate		122	....	...	...	....	No	.....	5.03
Ethyl Butyrate		78	85	...	...	....	No	0.879	4.00
Ethyl Chloride	Chloroethane	–58	–45	3.6	14.8	....	No	0.910	2.22
Ethylene		gas	....	3.02	34	1009	No	.....	0.975
Ethylene Chlorohydrin		....	140	...	...	....	No	1.213	2.78
Ethylene Diamine		93	110	...	...	....	No	0.890	2.07
Ethylene Dichloride	Dichloro Ethane-1, 2	56	65	6.2	15.9	775	No	1.258	3.42
Ethylene Glycol	Glycol	232	240	...	...	775	No	1.113	2.14
Ethylene Oxide		....	....	3	80	804	No	0.887	1.52
Ethyl Formate		–4	10	3.5	16.5	....	No	0.922	2.55
Ethyl Glycol Acetate		117	....	...	...	....	No	.....	4.55
Ethyl Lactate		115	....	...	...	....	No	1.03	4.41
Ethyl Mercaptan	Ethyl Sulfhydrate	....	....	2.8	18.2	570	..	0.839	2.11
Ethyl Nitrate	Nitric Ether	50	50	3.8	...	....	No	1.105	3.14
Ethyl Nitrite	Nitrous Ether	–31	–30	3.01	>50	....	No	0.900	2.59
Ethyl Oxalate		....	....	...	...	....	No	1.080	5.04
Ethyl Phthallyl Ethyl Glycollate		365	385	...	...	....	..	>1	....
Ethyl Propionate		54	....	...	...	....	No	0.891	3.52
Ethyl Silicate		....	125	...	...	....	..	0.936	7.22
Ethyl p-Toluene Sulfonamide		260	380	...	...	....	..	.....	....
Ethyl p-Toluene Sulfonate		316	....	...	...	....	..	.....	....
Formaldehyde, (gas)	Methanal	....	....	...	...	806	No	....	1.03
(Soln. of gas in water)		130	200	...	...	....	No	.....	...
Formic Acid		156	....	...	...	....	..	1.218	1.59
Fuel Oil No. 1	Range Oil	100–165	....	...	...	490	No	<1	....
Fuel Oil No. 2		110–190	....	...	...	494	No	<1	..
Fuel Oil No. 3		125–200	....	...	...	498	No	<1	....
Fuel Oil No. 4		150+	250	...	...	505	No	<1	....
Fuel Oil No. 5		150+	....	...	...	....	No	<1	....
Fuel Oil No. 6		150+	320	...	...	765	No	<1	....
Furfural		140	155	2.1	...	739	No	1.159	3.31

TABLE 6.1. PROPERTIES OF FLAMMABLE LIQUIDS, GASES AND SOLIDS—*Continued*

NAME	SYNONYMS	Flash Point °F		Explosive Limits % by Vol. in Air		Autoignition Temp. °F.	Susceptibility to Spontaneous Heating	Specific Gravity (Water = 1.00)	Vapor Density (Air = 1.00)
		Closed Cup	Open Cup	Lower	Upper				
Furfuryl Alcohol	Furfuryl Carbinol	....	....	...	...	915	..	1.129	3.37
Gas, Blast Furnace		....	....	35	74	....	No	.....	....
Gas, Coal Gas		....	....	5.3	31	1200	No	.....	....
Gas, Illuminating		....	....	5.3	31	1094	No	.....	....
Gas, Natural		....	....	4.8	13.5	....	No	.....	....
Gas, Oil Gas		....	....	6.0	13.5	637	No	.....	....
Gas, Producer		....	....	20.7	73.7	....	No	.....	....
Gas, Water		....	....	9.0	55.0	....	No	.....	....
Gas Oil		150+	....	...	...	640	No	<1	....
Gasoline		-50	....	1.3	6	495	No	0.75	3–4
Glycerine	Glycerol	320	350	...	...	739	No	1.26	3.17
Glyceryl Triacetate	Triacetin	280	295	...	...	....	No	1.161	7.52
Glycol Diacetate	Ethylene Acetate	....	220	...	...	....	No	1.100	4.53
Heptane-n		25	....	1	6	452	No	0.683	3.45
Hexane-n		-7	....	1.25	6.90	477	No	0.661	2.97
Hexyl Acetate	Ethyl Butyl Acetate	135	....	...	...	....	No	0.83	4.97
Hexyl Acetate	Methyl Amyl Acetate	113	....	...	...	....	No	0.855	4.97
Hexyl Alcohol-n	Hexanol-n	145	....	...	...	....	No	0.82	3.52
Hexyl Alcohol	Ethyl Butyl Alcohol	137	....	...	...	....	No	0.818	3.52
Hexyl Alcohol	Methyl Amyl Alcohol	114	....	...	...	....	No	0.804	3.52
Hydrocyanic Acid		0	....	5.6	40	1000	No	0.697	0.9
Hydrogen		gas	....	4.1	74.2	1076	No	.....	0.069
Hydrogen Sulfide		gas	....	4.3	45.5	....	No	.....	1.189
Hydroquinone		329	....	...	...	....	..	1.332	3.81
Isobutyraldehyde		-40	....	...	...	490	..	.813	....
Kerosene	No 1 Fuel Oil	100–165	....	...	...	490	No	<1	....
Lanolin	Wool Grease	460	560	...	...	833	Yes	<1	....
Lard Oil (Commercial)		395	....	...	...	833	Yes	<1	....
Lead Tetramethyl		....	....	1.8	...	....	..	1.995	9.20
Linseed Oil		435	535	...	...	820	Yes	0.93	....
Lubricating Oil, Cylinder		....	535	...	...	783	No	<1	....
Lubricating Oil, Light Machine		318	370	...	...	....	No	<1	....
Lubricating Oil, Motor		....	450	...	...	....	No	<1	....
Lubricating Oil, Spindle		169	200	...	...	....	No	<1	....
Lubricating Oil, Turbine		....	400	...	...	700	No	<1	....
Magnesium (Powder or Chips)*		....	....	...	...	....	No	.....	....
Manganese (Powder)*		....	....	...	...	....	No	.....	....
Menhaden Oil		435	....	...	...	828	Yes	0.927	....
Mesityl Oxide		87	....	...	...	....	..	0.858	3.40
Metaldehyde	m-Acetaldehyde	97	135	...	...	....	No	....	6.06
Methane	Marsh Gas	gas	....	5.3	13.9	999	No	.....	0.554
Methoxy Ethyl Phthalate	Methox	275	370	...	...	....	No	.....	...
Methyl Acetate		15	20	4.1	13.9	935	No	0.925	2.56
Methyl Acetoacetate		180	..	...	...	...	No	1.077	4.00
Methyl Alcohol	Methanol	54	60	6.0	36.5	878	No	0.792	1.11

Table 6.1. Properties of Flammable Liquids, Gases and Solids—*Continued*

NAME	SYNONYMS	Flash Point °F		Explosive Limits % by Vol. in Air		Autoignition Temp. °F.	Susceptibility to Spontaneous Heating	Specific Gravity (Water = 1.00)	Vapor Densit (Air = 1.00)
		Closed Cup	Open Cup	Lower	Upper				
Methyl Amine		0	10	...	...	....	No	0.699	....
Methyl Bromide	Bromomethane	practically non-flammable		13.5	14.5	....	No	1.732	3.27
Methyl n-Butyl Ketone	Hexanone	....	95	1.22	8.0	....	No	0.830	3.45
Methyl iso-Butyl Ketone	Hexanone	73	....	...	...	....	No	0.803	3.45
Methyl Butyrate		57	....	...	...	....	No	0.898	3.52
Methyl Carbitol		....	200	...	...	....	No	1.035	4.14
Methyl Cellosolve		107	115	...	...	551	No	0.966	2.62
Methyl Cellosolve Acetate		132	140	...	...	....	No	1.005	4.07
Methyl Chloride	Chloromethane	gas	....	8.2	19.7	....	No	0.92	1.78
Methyl Cyclohexane		25	....	1.15	...	....	No	0.770	3.38
Methyl Cyclohexanol	Methyl Hexalin	154	....	...	...	....	No	0.933	3.93
Methyl Cyclohexanone		118	....	...	...	....	No	0.925	4.86
Methyl Cyclohexyl Acetate		147	....	...	...	....	No	.....	5.37
Methylene Chloride	Dichloromethane	practically non-flammable		...	...	1224	No	1.336	2.93
Methyl Ethyl Ether		–35	....	2	10.1	374	No	0.697	2.07
Methyl Ethyl Ketone		30	....	1.81	11.5	....	No	0.805	2.41
Methyl Formate		–2	....	5.0	22.7	840	No	0.975	2.07
Methyl Glycol		97	....	...	...	....	No	.....	2.62
Methyl Glycol Acetate		111	....	...	...	....	No	.....	4.07
Methyl Phthallyl Ethyl Glycollate		375	380	...	...	....	No	>1	....
Methyl Propionate		28	....	...	...	....	No	0.915	3.03
Methyl n-Propyl Ketone	Pentanone	....	60	1.55	8.15	....	No	0.812	2.96
Methyl Salicylate	Oil of Wintergreen	214	225	...	...	850	No	1.182	5.24
Mineral Seal Oil (Typical)		170	255	...	...	....	No	.....	....
Monocresyl Diphenyl Phosphate		450	450	...	...	....	No	>1	....
Monofluorotrichloromethane	F-11	non-flammable		...	...	....	No	.....	....
Mustard Oil		566	....	...	...	....	Yes	1 02	....
Naphtha, Coal Tar	Hi-Flash Naphtha	100–110	....	...	...	900–950	No	<1	....
Naptha, Safety Solvent	Stoddard Solvent, Mineral Spirits	100–110	....	1.1	6.0	450–500	No	<1	....
Naphtha, V. M. & P.	Benzine	20–45	....	1.2	6.0	450–500	No	<1	....
Naphthalene		174	190	0.9	...	1053	No	1.145	4.42
Naphthol, beta		307	340	...	...	....	No	1.22	4.97
Naphthylamine-alpha		315	....	...	...	....	No	1.171	4.93
Neatsfoot Oil		470	....	...	...	828	Yes	0.92	....
Nicotine		....	....	0.75	4.0	471	..	1.009	5.61

TABLE 6.1. PROPERTIES OF FLAMMABLE LIQUIDS, GASES AND SOLIDS—*Continued*

NAME	SYNONYMS	Flash Point °F		Explosive Limits % by Vol. in Air		Autoignition Temp. °F.	Susceptibility to Spontaneous Heating	Specific Gravity (Water = 1.00)	Vapor Density (Air = 1.00)
		Closed Cup	Open Cup	Lower	Upper				
p-Nitroaniline	Paranitraniline	390	390	...	...	....	..	1.437	....
Nitrobenzene		190	....	...	...	924	..	1.2	4.25
p-Nitrochlorobenzene		261	....	...	...	....	..	1.52	5.43
Nitroethane		82	106	...	...	....	..	1.052	2.58
Nitroglycerin	Glyceryl Trinitrate	Explodes	....	...	...	518	No	1.601	7.84
Nitromethane		....	112	...	...	....	..	1.139	2.11
Nitronaphthalene-alpha		327	....	...	...	....	..	1.331	5.96
1-Nitropropane		....	120	...	...	....	..	1.003	3.06
2-Nitropropane		....	103	...	...	....	..	0.992	3.06
p-Nitrotoluene		223	....	...	...	....	..	1.286	4.72
m-Nitro p-Toluidine		315	345	...	...	....	..	1.312	5.24
Nonane-n		88	....	0.74	2.9	....	No	0.718	4.41
Octane-n		56	....	0.84	3.2	450	No	0.706	3.86
Octyl Acetate-n		180	....	...	...	....	No	0.885	5.93
Octyl Alcohol-n		178	....	...	...	....	No	0.827	4.48
Octyl Aldehyde		125	....	...	...	....	No	0.821	4.41
Oleic Acid	Red Oil	372	....	...	...	685	Yes	0.891	....
Oleo Oil		....	....	...	...	....	Yes	0.915	....
Olive Oil		437	....	...	...	826	Yes	0.910	....
Ozokerite		236	315	...	...	....	No	0.95	....
Palm Oil		421	....	...	...	650	Yes	0.92	....
Paraffin Wax		390	430	...	...	473	No	0.9	....
Paraformaldehyde		158	200	...	...	....	No	.....	....
Peanut Oil		540	....	...	...	833	Yes	0.92	....
Pentane-n		<-40	....	1.4	8.0	588	No	0.631	2.48
Perilla Oil		522	....	...	...	....	Yes	0.93	....
Petroleum, Crude		20-90	....	...	...	....	No	<1	....
Petroleum Ether		-50	....	1.4	5.9	475	No	0.64	2.50
Phenanthrene		....	....	...	...	....	No	1.063	6.14
Phenol	Carbolic Acid	175	185	...	...	1319	No	1.07	3.24
Phenyl Cellosolve		....	250	...	...	....	No	1.109	....
p-Phenylene Diamine		312	310	...	...	....	No	.....	3.72
Phenyl Ethyl Alcohol		216	....	...	...	....	No	1.024	4.21
Phosphorous (Red)		....	....	...	...	500	No	2.30	....
Phosphorous (Yellow)		....	....	...	...	86	No	1.82	....
Phosphorous Sesquisulfide		....	....	...	...	212	No	2.03	....
Phthalic Anhydride		305	330	...	...	....	No	1.527	5.10
Picric Acid	Trinitrophenol	Explodes	....	...	...	<572	No	1.763	7.90
Pine Oil		172	175	...	...	....	Yes	0.86	....
Pine Pitch		285	....	...	...	....	Yes	.....	....
Pine Resin	Colophony	370	430	...	...	....	Yes	1.08	....
Pine Tar		130	255	...	...	671	Yes	.....	....
Pine Tar Oil		144	....	...	...	....	Yes	0.862	....
Potassium*		....	....	...	...	....	No	0.862	....
Potassium Xanthate		205	....	...	9.5	....	No	1.558	....
Propane		gas	....	2.37	9.5	871	No	.....	1.56
Propyl Acetate-n		58	....	2.0	...	....	No	0.886	3.52
Propyl Acetate-iso		43	45	2.0	...	860	No	0.877	3.52

TABLE 6.1. PROPERTIES OF FLAMMABLE LIQUIDS, GASES AND SOLIDS—*Continued*

NAME	SYNONYMS	Flash Point °F		Explosive Limits % by Vol. in Air		Autoignition Temp. °F.	Susceptibility to Spontaneous Heating	Specific Gravity (Water = 1.00)	Vapor Densit (Air = 1.00)
		Closed Cup	Open Cup	Lower	Upper				
Propyl Alcohol-n		59	85	2.5	...	812	No	0.804	2.07
Propyl Alcohol-iso		53	60	2.5	...	852	No	0.789	2.07
Propyl Alcohol-sec.	Dimethyl Carbinol	67	....	...	...	....	No	0.79	2.07
Propyl Benzene-n		86	....	...	...	....	No	0.862	4.14
Propyl Benzene-iso	Cumene	102	....	...	...	....	No	0.864	4.14
Propyl Chloride-n	1-chloropropane	....	....	2.6	10.5	....	..	0.890	2.71
Propylene		gas	....	2.0	11.1	....	No	.....	1.49
Propylene Chlorohydrin		125	125	...	...	....	No	1.113	3.26
Propylene Dichloride	Dichloropropane-1, 2	59	65	3.4	14.5	1035	No	1.15	3.89
Propylene Glycol		210	225	...	...	....	No	1.040	2.52
Propylene Oxide		<20	....	...	...	....	No	0.859	2.00
Propyl Ether-iso		-18	-15	...	...	830	No	0.73	3.52
Propyl Formate-n		27	....	...	...	....	No	0.909	3.03
Propyl Formate-iso		22	....	...	...	....	No	0.873	3.03
Pyridine		68	....	1.8	12.4	1065	No	0.982	2.73
Pyrocatechol	o-Dihydroxy Benzene	261	....	...	...	....	No	1.344	3.79
Quenching Oil		365	405	...	...	....	No	0.9	....
Rape Seed Oil		325	550	...	...	836	Yes	0.915	....
Resorcinol	m-Dihydroxy Benzene	261	....	...	...	....	No	1.272	3.79
Rosin Oil		266	....	...	...	648	Yes	0.98–1.1	....
Sodium*		....	....	...	...	....	No	0.97	....
Sodium Formate		....	....	...	...	....	No	1.919	....
Soya Bean Oil		540	....	...	...	833	Yes	0.925	....
Stearic Acid		385	425	...	...	743	Yes	0.847	9.80
Styrene		90	....	1.1	6.1	914	..	0.907	3.60
Sulfur		405	440	...	...	450	No	2.046	....
Sulfur Chloride		245	None	...	...	453	No	1.687	3.31
Tallow		509	....	...	...	....	Yes	0.895	....
Tallow Oil		492	....	...	...	....	Yes	0.914	....
Tannic Acid		....	390	...	...	....	No	.....	....
Tartaric Acid	Racemic Acid	....	410	...	...	....	No	1.667	....
Terphenyl-o		....	325	...	...	....	..	1.14	7.95
Terphenyl-m		....	375	...	...	....	..	1.164	7.95
Terphenyl-p		....	405	...	...	....	..	1.236	7.95
Tetrachloroethylene	Perchlorethylene	non-flammable		...	...	....	No	1.623	5.72

TABLE 6.1. PROPERTIES OF FLAMMABLE LIQUIDS, GASES AND SOLIDS—*Continued*

NAME	SYNONYMS	Flash Point °F		Explosive Limits % by Vol. in Air		Autoignition Temp. °F.	Susceptibility to Spontaneous Heating	Specific Gravity (Water = 1.00)	Vapor Density (Air = 1.00)
		Closed Cup	Open Cup	Lower	Upper				
Tetradecane		212	....	0.5	...	....	No	0.765	6.83
Tetraethylene Glycol		....	345	...	...	....	No	1.126	....
Tetrahydronaphthalene	Tetralin	171	180	...	...	....	No	0.973	4.55
Tin Tetramethyl		....	....	1.9	...	....	No	1.314	....
Toluene	Toluol	40	45	1.27	7.0	1026	No	0.866	3.14
o-Toluidine	2-Methyl Aniline	185	....	...	...	900	No	0.999	3.90
p-Toluidine	4-Methyl Aniline	188	205	...	...	900	No	0.973	3.90
o-Tolyl p-Toluene Sulfonate		363	....	...	...	....	..	......	....
Transil Oil	Transformer Oil	...	295	...	...	....	No	0.9	....
Tributyl Citrate		315	365	...	...	695	..	.....	....
Tributyl Phosphate		....	295	...	...	....	No	0.973	8.86
Trichloroethylene		non-flammable		...	...	....	No	1.47	4.53
o-Tricresyl Phosphate		460	504	...	...	....	No	.....	....
Triethanolamine		355	365	...	...	....	No	1.13	5.14
Triethylene Glycol	Dicaproate	350	385	...	...	....	No	1.125	5.17
Triethylene Tetramine		....	260	...	...	....	No	0.982	....
Triglycol Dichloride		....	250	...	...	....	No	1.197	....
Triisopropanolamine		....	305	...	...	....	No	1.020	....
Triphenyl Phosphate		428	....	...	...	....	No	.....	....
Tung Oil	China Wood Oil	552	....	...	...	855	Yes	0.94	....
Turkey Red Oil		476	....	...	...	833	No	.....	....
Turpentine		95	....	0.8	...	488	Yes	<1	....
Vinyl Acetate		18	30	...	...	800	No	.....	....
Vinyl Chloride		....	....	4	22	....	No	0.97	2.15
Vinyl Ether	Divinyl Ether	<-22	....	1.85	36.5	680	..	0.774	2.41
Whale Oil	Sperm Oil	446	....	...	...	....	Yes	0.925	....
o-Xylene	o-Xylol	63	75	1.0	...	924	No	0.88	3.66
o-Xylidine	o-Dimethyl Aniline	206	....	...	...	....	No	0.99	4.17
Zinc (Dust or Powder)*		....	....	...	...	....	No	.....	....
Zirconium (Powder)				.		550	No	.....	....

I.C.C. SHIPPING LABELS

Red —Flammable liquids with flash points at or below 80° F. and flammable compressed gases.

Yellow—Flammable solids (except explosives) and oxidizing materials (chlorates, permanganates, peroxides, nitrates).

White —Corrosive liquids (mineral acids).

Green —Non-flammable compressed gases.

Labels are required only for interstate shipments or for intrastate shipments by common carrier engaged in interstate or foreign commerce. Absence of a label does not necessarily mean that the material is non-hazardous.

TABLE 6.2. HALOGENATED HYDROCARBON SOLVENTS

Flash points of mixed solvents[3]

A	PER CENT A	B	PER CENT B	ORIGINAL FLASH POINT
				°F
Trichloroethylene	80	Naphtha (72°)	20	180
Trichloroethylene	75	Benzine	25	180
Trichloroethylene	50	Kerosene	50	90
Trichloroethylene	67	Benzene (benzol)	33	187–90
		Turpentine	100	120
Trichloroethylene	75–83	Turpentine	17–25	192–5
Trichloroethylene	50	Stoddard solvent	50	None at 202
Trichloroethylene	75	Acetone	25	Below 34
Trichloroethylene	95	Acetone	5	70
Trichloroethylene	90	Acetone	10	45
Trichloroethylene	95	Isopropyl alcohol	5	75
Trichloroethylene	90	Isopropyl alcohol	10	65
Trichloroethylene	95	*sec*-Butyl alcohol	5	105
Trichloroethylene	90	*sec*-Butyl alcohol	10	95
Trichloroethylene	95	*tert*-Butyl alcohol	5	80
Trichloroethylene	90	*tert*-Butyl alcohol	10	70
Trichloroethylene	100			None
Ethylene dichloride	100			Below 60
Ethylene dichloride	90	Chloroform	10	65
Ethylene dichloride	70	Chloroform	30	90
Ethylene dichloride	60	Chloroform	40	None
Ethylene dichloride	90	Carbon tetrachloride	10	70
Ethylene dichloride	80	Carbon tetrachloride	20	80
Ethylene dichloride	70	Carbon tetrachloride	30	None
Ethylene dichloride	90	Trichloroethylene	10	55
Ethylene dichloride	60	Trichloroethylene	40	65
Ethylene dichloride	40	Trichloroethylene	60	95
Ethylene dichloride	80	Methylene chloride	20	60
Ethylene dichloride	65	Methylene chloride	35	70
Ethylene dichloride	60	Methylene chloride	40	None
Dichloroethylene	100			50
Chloroform	100			None
Carbon tetrachloride	100			None
Carbon tetrachloride	60	Acetone	40	Below 32
Carbon tetrachloride	70	Acetone	30	Below 32
Carbon tetrachloride	80	Acetone	20	57
Carbon tetrachloride	20	Toluene	80	57
Carbon tetrachloride	30	Toluene	70	74
Carbon tetrachloride	40	Toluene	60	Above 86

TABLE 6.3. FLASH POINTS OF ETHANOL-WATER MIXTURES

CONCENTRATION OF ETHANOL	FLASH POINT °F CLOSED CUP	FLASH POINT °F OPEN CUP
100% by vol.	56	65
95% " "	61	75
85% " "	67	80
70% " "	71	90
55% " "	77	95
40% " "	83	105
25% " "	94	115

TABLE 6.3a.* FLASH POINTS OF SOLVENTS AND PERCENTAGE OF CARBON TETRACHLORIDE TO PREVENT FLASHING AT 75 DEGREES FAH.

(By permission from National Safety Council's Industrial Data Sheet D-Gen. 13)

SOLVENT	FLASH POINT OF SOLVENT ALONE AT DEGREES FAHRENHEIT	PER CENT CARBON TETRACHLORIDE NECESSARY TO PREVENT FLASHING AT 75 DEGREES F.
High Test Gasoline	−20 (approx.)	80
Ordinary Motor Gasoline	−20 (approx.)	75
Various naphthas	0	70
	+20	55
	+40	40
	+60	25
Benzol	−16	70
Toluol	+46	35
Denatured Grain (Ethyl) Alcohol	+50 (approx.)	35
Methanol (Methyl or Wood Alcohol)	+30	85
Acetone	− 4	85
Amyl Acetate (Banana Oil)	+61	25
Ethyl Acetate	+32	65

* Courtesy Source: Stauffer Chem. Co.

TABLE 6.4.[3] IGNITABLE CONCENTRATIONS OF MIXED SOLVENTS

A	B	PER CENT A WHEN MIXTURE			
		Flashes and burns	Burns only	Ignites immediately	Will not ignite immediately
Acetylene tetrachloride	Ethyl acetate	20–40	50	60	70
Acetylene tetrachloride	Isopropyl alcohol	30	40–50	60	65
Carbon tetrachloride	Isopropyl alcohol			20	30
Carbon tetrachloride	Ethylene dichloride				25
Carbon tetrachloride	Ethyl acetate	30		40	50
Carbon tetrachloride	Benzene				70
Methylene chloride	Ethylene dichloride				40
Trichloroethylene	Benzene				67
Trichloroethylene	Stoddard solvent				50
Trichloroethylene	Ethylene dichloride				65

will not burn. Every car driver has direct experience with explosive ranges in his carburetor: if too much gas is fed, combustion is retarded and sometimes stopped altogether ("flooding").

It has been mentioned that the flash point varies with pressure, and this fact should be emphasized again, since the two are interdependent. Mitchell and Vernon[4] state that "the lower explosive limit line is simply a measure of flashpoint over the whole pressure range. Failing to give flashpoint as a function of pressure may create a false sense of security since the lower limit line shows that the point of entrance into the danger zone varies with pressure." They also point out that in all types of processing equipment, such as tanks, pipes, and wholly enclosed kettles, the use of flammable solvents should be undertaken only with full understanding of the fact that temperature and pressure are of as great concern as the explosive ranges themselves. The effect of less than normal atmospheric pressure may be to shift the lower explosive limit into the danger zone, so that a solvent that could be comparatively "safe" at 760 mm. may become highly flammable at 200 mm.

Monroe[5] was the first to recognize flammable liquids and gases as the cause of mysterious fires. He attributed these to static electricity which may develop when solvents flow through pipes or pass through a gaseous medium; when vapors pass into the air; and when a gas passes through a liquid medium.

Static electricity can be eliminated by the addition of a metallic soap. As an example, when 0.05 per cent of magnesium oleate is added to a solvent the electrical conductivity is increased to permit the elimination of electricity. Well-grounded pipe lines are another means of doing so. The greatest danger exists at the open end of a pipe, at which point a high potentiol may develop as the liquid leaves the pipe. To avoid this possible occurrence the liquid should not be permitted to spray, and should a high potentiol develop it can be neutralized by ionizing the air wish ultraviolet light or x-ray. A further aid would be to humidify the air.

Safe Solvents

Examination of the data in the foregoing tables will show that as a rule pure hydrocarbons and ethers tend to have low flash points and are likely to be hazardous. An effective method of reducing this hazard, and thus to increase the usefulness of these substances is by adding one or more halogen atoms (generally chlorine) to the molecule. The presence of chlorine is at least partially responsible for the non-flammability of "Freon" and carbon tetrachloride. Of course the extent of halogenation governs its effectiveness; partial halogenation has been widely used when the difficulties of completely halogenating were too great, as is the case of solvents of high molecular weight.[7] Aromatic compounds are somewhat more difficult to chlorinate than aliphatic.

Table 6.5[7] gives data showing the effect on flash point of the number of chlorine atoms per molecule. It is interesting to note that benzene, with no halogen atoms, had a flash point of 12° F by this method, and that the fully chlorinated hexachlorobutadiene, with 6 chlorine atoms, had no flash or fire point.

TABLE 6.5. EFFECT OF CHLORINATION ON FLAMMABILITY OF HYDROCARBONS

FLUID AND SOURCE	ATOMS OF CHLORINE PER MOLECULE	VISCOSITY, Cs. AT 100°F	FLASH POINT (C.O.C.), °F	FIRE POINT (C.O.C.), °F
Benzene	0	0.58	12[a, b]	. . .
Chlorobenzene	1	0.59	90[a, b]	. . .
o-Dichlorobenzene	2	0.84	165[b]	. . .
1,2,4-Trichlorobenzene (Hooker)	3	1.1	260	None[d]
Cumene (isopropylbenzene)	0	0.72	. . .	. . .
Trichlorocumene (Hooker)	3	2.3	235	430
Trichlorodiphenyl (Aroclor 1242)	3	17.7	350	633[d]
Tetrachlorodiphenyl (Aroclor 1248)	4	45.4	380	None
Diphenyl ether	0	2.6	265	275
Chlorodiphenyl ether (Dow)	1	3.0	260[d]	335[d]
Dichlorodiphenyl ether (Dow)	2	4.9	300[d]	465[d]
Trichlorodiphenyl ether (Dow)	3	8.7	325[d]	4901
Pentachlorodiphenyl ether (Hooker)	5	. . .	. . .	. . .
Ethylbenzene	0	0.61	75[a, b]	. . .
Polychloroethylbenzene (Du Pont)	4.5	6.8	325	565
Chloronaphthalene (Halowax 1000)	1.3	2.3	285	345
Hexachlorobutadiene (Hooker)	6	1.48	None	None

[a] Tag closed cup flash point.

[b] (*3*)

[d] Manufacturer's data.

Stoddard's solvent, specified for use in the dry-cleaning industry, has a flash point of 100–110° F and is therefore reasonably safe. A few entirely noncombustible solvents exist, and here again halogen content evidently plays the leading role.[6]

Polysiloxane fluids (silicone or organic silicon derivatives) have been investigated for possible use in lubrication and hydraulics because of their high resistance to thermal oxidation and their low temperature coefficients

TABLE 6.6. Non-Flammable Liquids

Methylene chloride		(none at ordinary Temperature)	1.8	5.37
Trichlorethylene	1–2	Vapor, at high temp., under certain conditions, forms explosive mixtures	3.8	4.53
Carbon tetrachloride	0	Non-combustible	3.0	5.32
Tetrachlorethylene	0			5.72
Tetrachlorethane	0			
Ethylene Dibromide	0		33.0	5.79

Note: For many of the newer solvents, no flammability ratings have as yet been assigned by the Underwriters' Laboratories.

of viscosity.[7] The flammability of these compounds is quite low compared with petroleum oils of the same viscosity, the flash points ranging from 200 to 600° F.

Toxicity

Toxicity is a relative term that usually refers to substances that are poisonous or harmful in very low concentrations. Thus arsenic is classified as a poison and table salt is not, though it may become so if an abnormally high concentration develops in the body. The point is that substances called poisons are toxic at minute concentrations; and though many substances can be toxic, the concentration required for this effect is comparatively high. For example, the intake of only a few milligrams of arsenic or other active poisons would probably be fatal, but a dose of as much as 15 or 20 grams of table salt would probably be necessary to cause acute distress.

In considering solvents as toxic agents then, the maximum allowable concentration is taken as the index; this has been defined[9] "the upper limit of concentration of a contaminant in the air which will not cause injury to an individual exposed continuously during the working day and for indefinite periods of time." This is usually expressed as so many parts of vapor per million parts of air (p.p.m.). The Chemical Safety Data Sheets issued by the Manufacturing Chemists' Association (Washington, D. C.) give complete details as to the type of hazards encountered with all the most widely used solvents, including oral intake. However, in speaking of the toxic hazards of a solvent, the vapor concentration to which workers are exposed is usually implied, rather than accidents involving swallowing of the liquid. Poisoning caused by inhalation of solvent vapors or external bodily contact may be either acute, subacute, or chronic. An indication of the major symptoms encountered in these three states is given below.

Acute poisoning may cause:

- Stiff leg muscles
- Headache
- Dizziness
- Forehead pressure
- Irritation of mucous membranes
- Nausea
- Narcosis
- Hysteria
- Blindness (methanol)
- Circulatory failure (trichloroethylene)
- Respiratory failure (benzene)
- Death

Subacute poisoning may cause:

- Fatigue
- Headache
- Dizziness
- Eye inflammation
- Visual disturbances
- Nausea
- Jaundice
- Liver dysfunction
- Nerve paralysis
- Heart fibrillation

Chronic poisoning may cause:

- Anemia
- Blood cell damage (benzene)
- Nerve damage
- Dermatitis ⎫ benzene
- Skin dryness ⎭ trichloroethylene

The maximum allowable concentration of commonly used solvents is given in Tables 6.7[10] and 6.8. Portable gas analyzers are available for obtaining quick and accurate measurements of vapor concentrations in the field, thus eliminating cumbersome and inaccurate sampling techniques.[10] Many large plants have installed solvent vapor recovering systems in recent years, and these, besides being economically advantageous, tend to keep free vapors at a minimum. The solvent vapors are received into a hood and passed over beds of activated carbon from which they are subsequently recovered by steaming.[11]

An excellent and detailed treatment of the physiological effects of toxic vapors is contained in "Noxious Gases," by the late Yandell Henderson

(Text continued on page 214)

TABLE 6.7. Maximum Allowable Concentration of Some Common Solvents[10]

GASES OR VAPORS	MAXIMUM ALLOWABLE CONCENTRATION	AUTHORITY
Acetone	500	California
Acrolein	1	N. J.
Acrylonitrile	20	N. J.
Ammonia	100	N. J. & Mass.
Amyl Acetate	200	N. J. & Mass.
Amyl Alcohol	55	Flury
Aniline	5	N. J. & Mass.
Arsine	.05	N. J. & Mass.
Benzene (Benzol)	35	N. J.
Bromine	.15	Dalla Valle
Butanol	100	California
Butyl Acetate	200	N. J. & Mass.
Butyl Alcohol	200	N. J.
Carbon Disulfide	20	N. J.
	15	Mass.
	1	Calif.
Carbon Monoxide	100	N. J. & Mass.
Carbon Tetrachloride	50	N. J. & Mass
Cellosolve	500	Dalla Valle
Chloroform	100	California
Chlorine	1	Massachusetts
Chlorodiphenyls	1	Massachusetts
Chloronaphthalene	1–5	Massachusetts
Dichloroethyl Ether	15	Mass. & Calif.
Dichloromethane	288	Flury
Dichlorobenzene	75	N. J. Mass. & Cal.
Dimethylaniline	5	N. J.
Dioxanes	1000	N. J.
Ether	400	Flury
Ethyl Acetate	139	Mass.
Ethyl Alcohol	250	Flury
Ethylbenzine	1000	Calif.
Ethyl Bromide	2000	Dalle Valle
Ethyl Chloride	20000	9–10
Ethyl Ether	400	Mass. & Calif.
Ethylene Dichloride	75	N. J. & Mass.
Ethylene Oxide	250	Dalla Valle
Ethyl Silicate	500	12
Formaldehyde	5	Mass.
Gasoline (Petroleum)	1000	N. J. & Mass.
Hydrochloric Acid	10	N. J. & Mass.
Hydrogen Chloride	10	N. J. & Mass.
Hydrogen Cyanide	20	N. J. & Mass.
Hydrogen Fluoride	1.5	N. J. & Mass.
Hydrogen Sulfide	20	N. J. & Mass.
Methyl Acetate	82	Flury

TABLE 6.7.—*Continued*

GASES OR VAPORS	MAXIMUM ALLOWABLE CONCENTRATION	AUTHORITY
Methyl Alcohol	200	N. J. & Mass.
Methyl Bromide	100	Dalla Valle
Methyl Chloride	500	Calif.
Methylethyl Ketone	3000	Dalla Valle
Methyl Formate	1500	Dalla Valle
Methylpropyl Ketone	1500	Dalla Valle
Monochlorobenzene	75	Cal. N. J. & Mass.
Mononitrotoluene	5	N. J.
Nitrobenzene	5	N. J. & Mass.
Nitrous fumes	10	Calif. & Mass.
Nitrogen Oxides	10	N. J. & Mass.
Ozone	1	Mass.
Pentachloroethane	2.4	Flury
Perchloroethane	30900	(Kills most animals in short time)
Petroleum Naphthas	1000	N. J.
Phosgene	1	N. J. & Mass.
Phosphorus Trichloride	.7	3-6-7-23-32
Phosphine	1	N. J.
Propyl Acetate	82	Flury
Sulfur Dioxide	10	N. J. & Mass.
Sulfur Trioxide	2	3
Tetrachloroethane	5	N. J. & Mass.
Tetrachloroethylene	200	Calif. & Mass.
Toluene (Toluol)	200	N. J. & Mass.
Toluidine	6	6
Trichloroethylene	200	N. J. & Mass.
Turpentine	200	N. J. & Mass.
Vinyl Chloride	5000	Dalla Valle
Xyline (Xylol)	200	N. J. & Mass.
	100	California

TABLE 6.8. COMPARATIVE TOXICITY OF HALOGENATED HYDROCARBONS FROM ALLOWABLE CONCENTRATIONS FOR PROLONGED EXPOSURE. CARBON TETRACHLORIDE TAKEN AS 1. BASED ON CONCENTRATION BY VOLUME OF AIR.[8]

LEHMANN AND FLURY		MORE WIDELY ACCEPTED AMERICAN FIGURES (1940)	
1. Dichloromethane	0.11	1. Ethyl chloride	0.05
2. Methyl chloride	0.13	2. Ethyl bromide	0.06
3. Trichloroethylene	0.17	3. Methyl chloride	0.20
4. Trichloroethane	0.18	4. Trichloroethylene	0.50
5. Tetrachloroethylene	0.22	5. Tetrachloroethylene	0.50
6. Chloroform	0.80	6. Chloroform	1.00
7. Carbon tetrachloride	1.00	7. Carbon tetrachloride	1.00
8. Pentachloroethane	13.50	8. Methyl bromide	2.00
9. Tetrachloroethane	21.50	9. Tetrachloroethane	10.00

and Howard W. Haggard, both of Yale University,[8] from which the following tables of physiological response data are taken.

TABLE 6.9. PHYSIOLOGICAL RESPONSE TO VARIOUS CONCENTRATIONS OF PENTANE, HEXANE, HEPTANE, AND GASOLINE[8]

	PARTS OF VAPOR PER MILLION PARTS OF AIR
Pentane	
Exposure 10 min., no symptoms	5,000
Hexane	
Exposure 10 min., no symptoms	2,000
Exposure 10 min., dizziness	5,000
Heptane	
Exposure 6 min., slight dizziness	1,000
Exposure 4 min., dizziness	2,000 to 3,500
Exposure 4 min., marked dizziness, muscular incoördination, emotional disturbances	5,000
Exposure 15 min., similar symptoms after 4 min. exposure but persisting for 30 min. following exposure	5,000
Gasoline	
Maximum concentration allowable for prolonged exposure	1,000 to 1,500
Slight symptoms after several hours	1,250 to 2,500
Maximum concentration tolerable for 1 hr.	4,000 to 7,000
Dangerous for short exposure	10,000 to 20,000
Fatal for short exposure	20,000 to 30,000

TABLE 6.10. PHYSIOLOGICAL RESPONSE TO VARIOUS CONCENTRATIONS OF KETONES[8]

	PARTS OF VAPOR PER MILLION PARTS OF AIR
Methyl ethyl ketone	
Maximum concentration allowable for prolonged exposure	Below 3,000
Slight symptoms after exposure of several hours	3,000
Maximum concentration safe for short exposure	10,000
Dangerous for short exposure	50,000 to 100,000
Methyl propyl ketone	
Maximum concentration allowable for prolonged exposure	Below 1,500
Slight symptoms after exposure of several hours	1,500
Maximum concentration safe for short exposure	5,000
Dangerous for short exposure	30,000 to 50,000

TABLE 6.10. PHYSIOLOGICAL RESPONSE TO VARIOUS CONCENTRATIONS OF KETONES[8] (*Continued*)

	PARTS OF VAPOR PER MILLION PARTS OF AIR
Methyl butyl ketone	
Maximum concentration allowable for prolonged exposure	Below 1,000
Slight symptoms after exposure of several hours	1,000
Maximum concentrations safe for short exposure	3,000
Dangerous for short exposure	10,000 to 20,000

TABLE 6.11. PHYSIOLOGICAL RESPONSE TO VARIOUS CONCENTRATIONS OF HALOGENATED HYDROCARBONS. CONCENTRATION IN PARTS OF VAPOR PER MILLION PARTS OF AIR[8]

	KILLS ANIMALS IN A SHORT TIME	DEEP NARCOSIS, 30 MINUTES	SLIGHT SYMPTOMS, 8 HOURS	ESTIMATED ALLOWABLE CONCENTRATION, PROLONGED EXOSURE	
Methyl chloride	225,000	150,000	750	242	500
Methyl bromide	30,000	—	110	—	50
Dichloromethane	—	20,000	—	288	—
Chloroform	53,000	13,000	4,000	40	100
Carbon tetrachloride	65,000	22,000	1,600	32	100
Ethyl chloride	225,000	66,000	20,000	—	2,000
Ethyl bromide	150,000	—	2,300	—	1,700
Dichloroethane	150,000	12,000	1,000	494	100
Trichloroethane		8,000		183	—
Tetrachloroethane	7,300	3,200		1.5	10
Pentachloroethane	9,600	3,200		2.4	—
Vinyl chloride	300,000	—	7,500	—	—
Trichloroethylene	37,000	13,500		186	200
Tetrachloroethylene	—	8,000		147	200

TABLE 6.12. ACUTE PHYSIOLOGICAL RESPONSE TO VARIOUS CONCENTRATIONS* OF BENZENE[8]

	PARTS OF BENZENE VAPOR PER MILLION PARTS OF AIR
Slight symptoms after several hours	1,500 to 3,000
Maximum concentration that can be inhaled for 1 hour without serious disturbance	3,000 to 4,700
Dangerous to life in ½ to 1 hour	7,500
Rapidly fatal for even short exposure	19,000 to 20,000

* The concentrations given here are for immediate acute effects only; exposure of several hours or days to concentrations lower than those mentioned here may lead to chronic poisoning.

TABLE 6.13. PHYSIOLOGICAL RESPONSE TO VARIOUS CONCENTRATIONS OF ESTERS OF ORGANIC ACIDS[8]

		PARTS OF VAPOR PER MILLION PARTS OF AIR
Methyl formate		
Slight symptoms after several hours		1,500 to 2,000
Maximum concentration safe for short exposure		5,000
Dangerous for short exposure		15,000 to 25,000
Methyl acetate		
Maximum concentration allowable for prolonged exposure		83
Ethyl acetate		
Maximum concentration allowable for prolonged exposure		139
Dangerous for short exposure		10,000 to 20,000
Propyl acetate		
Maximum concentration allowable for prolonged exposure		83
Butyl acetate		
Maximum concentration allowable for prolonged exposure		100
Amyl acetate		
Maximum concentration allowable for prolonged exposure	*iso.*	47 to 400
	sec.	—
Slight symptoms after several hours	*iso.*	—
	sec.	2,000
Maximum concentration safe for short exposure	*iso.*	5,000 to 10,000
	sec.	5,000

TABLE 6.14. PHYSIOLOGICAL RESPONSE TO VARIOUS CONCENTRATIONS OF CARBON DISULFIDE[8]

	PARTS OF CARBON DISULFIDE PER MILLION PARTS OF AIR
Slight symptoms after several hours	300 to 400
Maximum concentrations that can be inhaled for 1 hour without serious disturbance	480 to 1,600
Dangerous after exposure of 30 minutes or 1 hour	1,000 to 3,850

Safety Measures

One of the most effective protective measures against both flammability and toxicity is the proper education of personnel. This point is often overlooked and it cannot be emphasized too greatly. Employees should be aware of the insidious nature of toxic fumes and of the symptoms resulting from over-exposure. No mechanical equipment can substitute for such safety education, for no matter how quickly a fire is extinguished or a worker resuscitated, it would have been better if the accident had not occurred. Employee education can be achieved by periodic lecture or instruction groups, by safety posters, and by careful daily checking of plant conditions by department supervisors.

Probably the most important preventive measure on the mechanical side is adequate ventilating equipment, including fans, blowers, and hoods; this equipment should be so planned as to insure keeping the air well below the maximum allowable concentration of the solvent vapor concerned. In the case of benzene, this is 35 p.p.m.; for carbon disulfide from 1 to 20 p.p.m.; and for carbon tetrachloride 50 p.p.m. All containers should be accurately labelled and leak-proof, with minimum chance of drip or spillage. Employees should be cautioned never to enter storerooms or other enclosures in which there has recently been a high concentration of solvent vapors without first thoroughly airing them; this includes peering into kettles or mixers. Goggles and protective aprons or clothing should be worn. Gas masks and emergency resuscitation equipment must be available.

Direct contact with benzene, trichloroethylene, etc., should be avoided, as prolonged exposure will cause dermatitis. This can be avoided by wearing gloves and by frequent washing after exposure. Protective creams and lotions are of little value, except those containing lanolin, which tends to supply the oils removed from the skin by these solvents.

If a person is overcome by toxic fumes, he should be at once removed to fresh air and resuscitated by artificial respiration or by an inhalator. A physician should be summoned immediately. Nothing should ever be given orally to an unconscious person. No attempt can be made here to give complete details; those interested are referred to the series of Chemical Safety Data Sheets previously mentioned, one of which is reproduced on the following pages.

CARBON DISULFIDE

Adopted 1947

Revised 1948

1. NAME

Chemical Names: Carbon Disulfide, Carbon Bisulfide
Common Names: Carbon Disulfide, Carbon Bisulfide
Formula: CS_2

2. PROPERTIES

2.1 **Grades:** Commercial or Technical, and USP

2.2 **Important Physical and Chemical Properties**

Physical State: Liquid.
Color: Clear, colorless liquid.
Odor: Almost odorless when pure; the commercial grade has a strong disagreeable odor, due to presence of sulfur compounds.
Specific Gravity at 20° C/4° C (68° F/39° F) (Water = 1): 1.263
Vapor Density (Air = 1): 2.63
Boiling Point (760 mm): 46.3° C (115° F)
Melting Point: −108.6° C (−163° F)
Flash Point (closed cup): −30° C (−22° F)
Explosive Limits (per cent by volume in air): 1 to 50
Ignition Temperature: 100° C (212° F)
Corrosive: Commercial grade slightly corrosive to some metals due to impurities.
Dangerously Reactive: No. However, it has an extremely low ignition temperature.
Hygroscopic: No.
Light Sensitive: Turns yellow when exposed to sunlight.

Vapor Pressure of Carbon Disulfide

Temperature		Vapor Pressure MM Mercury
°C	°F	
−78.2	−109	0.68
−42.6	−45	11.81
−25.35	−14	34.3
−21.5	−7	42.7
0	+32	127.0
11.54	53	211.3
19.7	67	294.3
46.3	115	760.0

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2.3 Hazardous Properties

2.3.1 *HEALTH HAZARDS*. Carbon disulfide is harmful by inhalation of the vapor, prolonged or repeated contact of the liquid with the skin, or by oral intake. (See 8. Health Hazards and Their Control.)

2.3.2 *FIRE HAZARD*. Carbon disulfide is a highly flammable volatile liquid with an extremely low ignition temperature. (See 6.2 Fire and Explosion Hazards.) Its vapor, when mixed with air or oxygen in certain concentrations, is highly flammable and explosive.

3. USUAL SHIPPING CONTAINERS

Carbon disulfide is classified by the Interstate Commerce Commission as an inflammable* liquid. As such, it must be packed in ICC specification containers when shipped by rail, water, or highway, and all of the ICC Regulations regarding loading, handling, and labeling must be followed. It must not be offered for transportation by rail express.

3.1 Type and Size

3.1.1 Glass bottles or metal cans, 5 pint maximum, in wooden barrels or kegs, ICC Spec. 11A or 11B.

3.1.2 Glass bottles, 1 pint maximum, or metal cans, 1 quart maximum, in fiber-board boxes 60 pounds maximum gross weight, ICC Spec. 12B.

3.1.3 Glass bottles, 5 pint maximum; or metal cans, 10 gallon maximum (ICC Spec. 2A), in wooden boxes, ICC Spec. 15A, 15B, 15C, 16A, or 19A.

3.1.4 Metal Drums, non-returnable, 5 gallon maximum, ICC Spec. 17E.

3.1.5 Metal barrels or drums, non-returnable, 55 gallon maximum, ICC Spec. 17C.

3.1.6 Metal barrels or drums, returnable, 55 gallon maximum, ICC Spec. 5 or 5A.

3.1.7 Tank cars, ICC Spec. 103, 104, 104A.

3.1.8 Tank trucks, ICC Spec. MC300, MC301, MC302, or MC303.

3.2 Label or Identification

3.2.1 Each container (including tank cars) should carry an identifying label or stencil.

3.2.2 Each package with inside container of 1 quart or larger capacity should carry a THIS SIDE UP label.

3.2.3 The Manufacturing Chemists' Association recommends the following in addition to, or in combination with, any label warnings required by statutes, regulations or ordinances.

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* While the term "inflammable" is used by the ICC, the preferred form "flammable" is used in this Data Sheet.

3.2.4 Each drum, and each box with an inside container, must bear the ICC red label for "inflammable" liquids.

3.2.5 Each tank car and each railroad car carrying one or more containers of carbon disulfide must bear the ICC DANGEROUS placard.

3.3 Disposal and Return Precautions

3.3.1 Before returning shipping containers to suppliers, observe usual precautions regarding complete drainage of contents and properly close all openings.

3.3.2 Follow ICC Regulations regarding condition of empty containers and labeling; and condition of empty cars and placard requirements before returning to the shipper.

3.3.3 Before returning bottles to the shipper, they must be stoppered, and the ICC red labels for "inflammable" liquids on the cases must be removed, obliterated, destroyed, or completely covered by a square white EMPTY label.

3.3.4 As soon as a tank car is completely unloaded, the unloading connections should be removed and all closures made tight.

3.3.5 Return empty tank cars as promptly as possible, in accordance with instructions received from the shipper. Shipper's routing instructions should always be followed strictly.

3.3.6 Non-returnable containers should be washed out thoroughly before scrapping.

4. UNLOADING AND EMPTYING

4.1 **Health Hazards.** Carbon disulfide is harmful by inhalation of the vapor, prolonged or repeated contact of the liquid with the skin, or by oral intake. (See 8. Health Hazards and Their Control.)

4.2 **Fire Hazard.** Carbon disulfide is a highly flammable volatile liquid. (See 6.2 Fire and Explosion Hazards.)

4.3 Tank Cars

4.3.1 Because of the high volatility and low ignition temperature of carbon disulfide, extreme caution is necessary when unloading tank cars of this liquid. For general and detailed instructions regarding the unloading of tank cars containing flammable liquids see MCA Manual Sheet TC-4 and the Regulations of the Interstate Commerce Commission, Sections 560 and 561. A few of these instructions are repeated and some other suggestions are added in the following.

4.3.2 Spot the car on a level track. Before any unloading is started, set car brakes, install standard rail clamps to block wheels, lock siding switches or provide derails, place blue warning flags fore and aft if necessary and ground the tank car and all of the pipe lines to be connected to same in accordance with MCA Manual Sheet TC-4.

4.3.3 Always unload through the dome connection. This is not only good practice, but is required by several state laws.

4.3.4 Never use air pressure for unloading. Use water displacement and approved pump (preferred) or inert gas displacement. As an added precaution, pumps should be surrounded by a shallow water basin so that any leaks around the pump casing or shaft may be immediately covered by water.

4.3.5 Use only non-sparking tools in or near the unloading area. Avoid striking fittings with tools or other hard objects.

4.3.6 Allow no smoking or flame producing devices in the area. Allow no exposed steam pipes or any device or equipment capable of producing a surface temperature greater than 93.3° C (200° F).

4.3.7 An approved flash screen (flame arrestor) should be placed over the tank car vent when relieving internal pressure.

4.3.8 The unloading dock and surrounding vapor area should be considered as a Class I hazardous location as defined by the National Electrical Code. All wiring, electrical apparatus and equipment such as lights, switches, receptacles, panel boards and portable lights (including flash lights) should be explosion-proof, conform with the requirements of Article 500 of the Code, and be approved for use in Class I Group D locations.

4.3.9 In case of spillage, clear and rope off the area, place warning signs and provide watchers until the product has evaporated. Watchers should be provided with adequate personal protective equipment (see 8.3). Do not allow carbon disulfide to run into or to be flushed into the sewer.

4.4 **Metal Barrels or Drums**

4.4.1 Drums should always be handled carefully to avoid damage.

4.4.2 Each shipment should be examined carefully for leaking drums. If any are found, they should be handled with particular care to prevent further leakage, and should be removed to a safe place where the leaking can be stopped by tightening the plug or by some other approved method. The contents of defective drums should be transferred to a sound container.

4.4.3 Keep all flame or spark producing devices away from drums during unloading.

4.4.4 Use only non-sparking tools. Avoid striking fittings with tools or other hard objects.

4.4.5 Before unloading, the drum and all piping should be electrically interconnected and grounded to prevent the accumulation of static electricity.

4.4.6 Drums should be unloaded by water displacement and approved pump. Under no circumstances should air or inert gas pressure be used. Drums are not pressure vessels.

4.4.7 If carbon disulfide is spilled, clear and rope off the area, place warning signs and provide watchers until the product has evaporated. If indoors, follow the same procedure while ventilating the room or building thoroughly. Watchers should be provided with adequate personal protective equipment (see 8.3).

4.5 Small Containers

4.5.1 Keep all flame or spark producing devices away during emptying.

4.5.2 If metal cans are involved, they should be grounded and electrically interconnected with the container being filled.

4.5.3 Use only non-sparking tools.

5. STORAGE

5.1 Hazards

5.1.1 *HEALTH HAZARDS.* Carbon disulfide is harmful by inhalation of the vapor, prolonged or repeated contact of the liquid with the skin, or by oral intake. (See 8. Health Hazards and Their Control.)

5.1.2 *FIRE HAZARD.* Carbon disulfide is a highly flammable volatile liquid. (See 6.2 Fire and Explosion Hazards.)

5.1.3 *CORROSION.* Tanks and containers used for the storage of carbon disulfide corrode very little.

5.1.4 *VOLATILITY.* Carbon disulfide is highly volatile.

5.1.5 *TEMPERATURE REQUIREMENTS.* Due to high vapor pressure, bulk storage should be under water and at or below normal temperatures. Drums should be sprayed with water in hot weather to keep the temperature low and the vapor pressure down.

5.2 Conditions of Storage

5.2.1 *TYPE OF CONSTRUCTION.* Structures in which carbon disulfide is stored should be non-combustible, and either open type or well ventilated at floor level. Storage should not be below grade.

5.2.2 *ISOLATION.* Carbon disulfide buildings should be isolated from other operations and buildings.

5.2.3 *BULK STORAGE.* Bulk storage of carbon disulfide should be under water in tanks, and drums should be under cover, with provisions for cooling the drums in hot weather.

5.2.4 *VAPOR PROOF REQUIREMENTS.* All electrical wiring, fixtures, and equipment should be installed in accordance with the requirements of the National Electrical Code for Class I, Group D hazardous locations.

5.2.5 *EXPLOSION VENTING.* Proper venting to relieve possible vapor-air explosions is extremely important.

5.2.6 *VENTILATION.* Avoid open handling, use safety cans. Carbon disulfide vapor is heavier than air, therefore downdraft mechanical ventilation is the most effective type if removal of vapor becomes necessary.

6. HANDLING

6.1 **Health Hazards.** Carbon disulfide is harmful by inhalation of the vapor' prolonged or repeated contact of the liquid with the skin, or by oral intake. (See 8. Health Hazards and Their Control.)

6.1.1 Although the American Standards Association suggests 20 ppm by volume in air as the *maximum* allowable concentration of carbon disulfide vapor for exposures not exceeding a total of eight hours daily, it is recommended, as an added precaution, because of the extremely hazardous nature of carbon disulfide, that the concentration not exceed 15 ppm for exposures of the order named.

6.2 **Fire and Explosion Hazards.** Carbon disulfide is a highly flammable volatile liquid with a low flash point, wide explosive range, and an extremely low ignition temperature—only 100° C (212° F). Contact with the surface of an ordinary electric light bulb will cause ignition. Carbon disulfide vapor, when mixed with air or oxygen in certain concentrations, is highly flammable and explosive.

6.2.1 Smoking and the carrying of matches in locations where carbon disulfide is stored, handled, or used should be prohibited.

6.2.2 No open flames or spark producing devices of any kind should be permitted in or around locations, buildings, or equipment where carbon disulfide is stored, handled, or used.

6.2.3 Non-sparking tools only should be used, and even then, care should be exercised that heavy blows are not struck where carbon disulfide vapor may be present.

6.2.4 The vapor is 2.63 times as heavy as air. It may travel some distance to a source of ignition, and flash back to the place of origin.

6.3 Spills and Leakage

6.3.1 Rope off and clear the area. Post warning signs, and watchers provided with adequate personal protective equipment. Keep all sources of ignition away. Allow the spilled carbon disulfide to evaporate.

6.3.2 If spilled or splashed on the body, remove immediately any clothing, gloves or shoes soaked with carbon disulfide and wash the body thoroughly.

6.4 Employee Education and Training

6.4.1 Safety in handling carbon disulfide (and other hazardous or corrosive chemical products) depends upon the effectiveness of employee education, training and supervision.

6.4.2 The education and training of the employees to work safely and use the personal protective equipment or other safeguards is a responsibility of supervision.

6.4.3 Employee education and training should emphasize the need of handling carbon disulfide according to methods outlined in this manual.

6.4.4 Before being placed on the job, new employees should be instructed thoroughly in the hazards of handling carbon disulfide. Older employees should be reinstructed periodically.

6.4.5 Each employee should know the location, purpose, use, and maintenance of personal protective equipment. (See 8.3) Each should also be taught when and how to use this equipment and be trained in its use.

6.4.6 Each employee should know the location of safety showers, bubbler drinking fountains, and hose lines. (See 6.10 Safety Showers and Washing Facilities.)

6.4.7 Only intelligent, dependable and properly trained employees should be given the responsibility of operating valves which control the movement of carbon disulfide to and from storage tanks, tank cars, and containers.

6.4.8 Employees should be trained to report to the proper authority all suspected leaks or equipment failures, and any signs of illness or skin difficulties.

6.4.9 Each employee should be trained what to do in an emergency and in first aid measures, and should realize the necessity for the prompt application of first aid in case of contact with carbon disulfide or exposure to the vapor.

6.4.10 Each employee should be taught the importance of proper personal habits as protection against carbon disulfide illness.

6.5 Personal Protective Equipment (See 8.3)

6.6 Engineering Controls

6.6.1 *LOCATION OF PROCESS.* No process involving the storage, handling, or use of carbon disulfide should be located near open flames, spark producing devices, or any exposed surfaces at a temperature above 93.3° C (200° F). Contact with the surface of an ordinary electric light bulb will cause ignition.

6.6.2 *DESIGN OF EQUIPMENT.* Processes should be designed so that carbon disulfide liquid and vapor are in a closed system at all times. Adequate ventilation should be provided whenever any vapor may be released. Due to the high toxicity and flammability of both the liquid and vapor, expert advice should be obtained on the design of processes using this chemical product.

6.6.3 *CHEMICAL TEST AND CHECKING.* The atmosphere in work rooms should be checked frequently for vapor concentration, since a concentration of over 15 ppm by volume in air for continuous eight hour exposure may constitute a health hazard.

6.6.4 *STATIC ELECTRICITY.* A very wide range (1 to 50 per cent) of carbon disulfide vapor-air mixtures are ignited easily by a spark of static electricity. Therefore, equipment should be designed to prevent the development of static insofar as possible and to prevent its accumulation. Electrical grounding should be installed throughout the premises to prevent the accumulation of static charges.

6.6.5 *ELECTRICAL EQUIPMENT.* Carbon dilsulfide occupancies should be considered as Class I hazardous locations as defined by the National Electrical Code. All wiring, electrical apparatus and equipment, such as lights, switches, receptacles, panel boards and portable lights (including flash lights) should be explosion-proof, conform with the requirements of Article 500 of the Code, and be approved for use in Class I Group D locations.

6.7 Ventilation

6.7.1 Workrooms should be provided with general ventilation of sufficient capacity to keep the concentration of vapor below 15 ppm by volume in air. See 8.2.1.

6.7.2 Carbon disulfide vapor is 2.63 times as heavy as air, therefore special ventilation of the downdraft or lateral type should be provided at locations where vapor may escape from open equipment. Special ventilation should be so designed that the vapor is drawn away from the operator's ace. It should be sufficient to keep the maximum concentration below 15 ppm and well below the lower limit of the explosive range.

6.8 Tank and Equipment Cleaning and Repairs

6.8.1 The hazardous nature of tank inspection, cleaning, or repairs requires that the foreman and crew be selected, trained, and drilled carefully. They should be fully familiar with the hazards, and the safeguards necessary for the safe performance of the work.

6.8.2 Wherever possible, enclosures should be cleaned from the outside, using clean-out doors.

6.8.3 All pipe lines into or out of the tank or other apparatus should be disconnected, preferably by removing a complete small section. Valves, cocks and blank flanges should not be relied upon.

6.8.4 Danger signs should be placed suitably to indicate when workmen are in the tank or other apparatus.

6.7.5 Be sure tank can be left by original entrance.

6.8.6 Lock all electrical switches in the off position, remove belts and completely safeguard against accidental starting of any agitating equipment or other moving parts located inside or adjacent to the tank entrance.

6.8.7 Before entering a tank, and during the course of the work, tests should be made by a qualified person to determine if further washing is necessary and to make sure that there is no oxygen deficiency, and that no harmful gases are present. Before directing men to enter a tank, an inspection of the interior should be made by the foreman, equipped with a hose-type gas mask, life belt, and life line; another person should be on guard during the inspection.

6.8.8 One man on the outside of the tank should keep the men in the tank under constant observation, and at least two men should be available to aid in rescue if any of the men in the tank are overcome.

6.8.9 A supplied air respirator or self-contained breathing apparatus, together with rescue harness and life line should always be located outside the tank entrance for rescue purposes, regardless of the type of respiratory equipment or air supply which is provided for employees inside the tank.

6.8.10 In addition to protecting the workmen actually engaged in cleaning and repairing the tank, attention should be paid to the protection of workers in nearby areas.

6.8.11 Cleaning or making repairs inside a tank may be hazardous even though the tank contained a non-toxic, non-flammable material. In addition to the precautions generally recommended for tank work, such as procurement of written approval of supervision, testing for oxygen deficiency, use of rescue harness or life belt and life line, provision of grounded equipment in good condition for portable lights and power tools, and stationing of thoroughly trained "watchers" outside of the tank entrance, additional precautions are recommended as follows:

(a) Drain the tank as completely as possible.

(b) Wash the interior of the tank thoroughly with running water and allow it to drain.

(c) Since carbon disulfide is frequently absorbed by scale in the inside of storage tanks and is not removed by flushing with water or by simple aeration, the carbon disulfide should be boiled out carefully. The recommended practice after the tank is drained, is to flush several times with water, fill the tank completely with water and then slowly raise the temperature by the addition of hot water. The manhole cover should be left open during this heating process and the water in all parts of the tank should be agitated occasionally to insure uniform distribution of the heat. This heating-up process should be carried out gradually and cautiously to avoid any possible sudden evolution of carbon disulfide vapor when the temperature of the water reaches the boiling point of carbon disulfide. If the tank and water are held at a temperature of approximately 60° C (140° F) for twenty-four hours, it can be assumed that all carbon disulfide has been driven off. Those not completely familiar with this process, should consult the carbon disulfide supplier, for special conditions may require modifications.

(d) Direct a stream of fresh air into the tank and ventilate until all traces of carbon disulfide have been completely evaporated and purged from the tank. It is good practice to keep a stream of fresh air flowing through the tank the entire time that anyone is in it, regardless of the type of respiratory equipment that is used.

6.9 Repackaging

6.9.1 *CONTAINERS.* See Section 3 for approved shipping containers. Handle in well ventilated area. Keep away from spark or flame producing devices. Electrically interconnect and ground metal containers, when pouring from one to another, or when filling from pipelines or storage tanks.

6.9.2 *LABELS.* (See 3.2)

6.10 **Safety Showers and Washing Facilities.** A readily accessible, well marked, deluge type safety shower, controlled by a quick opening valve, should be located in each area where carbon disulfide is handled. Small hose lines (garden hose) connected to a clean water line, and bubbler drinking fountains for washing the eyes, are recommended.

7. WASTE DISPOSAL

7.1 Small quantities of liquid waste, such as usually produced in laboratories, should be kept under water in an approved type safety can.

7.2 Waste carbon disulfide may be burned in a remote location if proper open containers are supplied and provision made for lighting with a train from the windward side, or a remote control lighting device is used. The chemical product will evaporate rapidly if poured on the ground at a safe location.

7.3 Under no condition should waste be flushed down sewers.

8. HEALTH HAZARDS AND THEIR CONTROL

This section includes not only recognized first aid procedures and information of interest to the layman, but also suggestions which may be of value to the attending physician.

8.1 Hazards

8.1.1 Carbon disulfide is harmful by inhalation of the vapor, prolonged or repeated contact of the liquid with the skin, or by oral intake.

8.1.2 The signs and symptoms of carbon disulfide poisoning are the result of injury to the nervous system. Poisoning is usually the result of long-continued exposure to relatively low concentrations of vapor.

8.1.3 The toxic symptoms of absorption by inhalation, in order of occurrence, are: nervousness, irritability, indigestion, bizarre dreams leading to insomnia, excessive fatigue, shortness of breath on slight or moderate exertion, loss of appetite, headache, and disturbances of sensation in the extremities. The signs of poisoning are: a waxy pallor; low blood pressure; tremors; unusual behavior (extreme excitement or depression); signs of injury to the nervous system with, in extreme cases, a masklike face, rigidity of the arms, neck and back, a tendency to hasten the gait in walking, loss of normal arm swing, slowness of movement, monotonous speech, excessive salivation and sweating, defective memory.

8.1.4 Poisoning from carbon disulfide is usually insidious.

8.1.5 *TOXIC EFFECTS FROM INHALATION*

8.1.5.1 *Acute Poisoning*

Acute poisoning is rare. Sudden exposure to concentrations of about 1,200 ppm may produce headache, nausea, dizziness, and if prolonged, lead to circulatory collapse and unconsciousness. A concentration of 4,000 ppm may be fatal after an exposure period of one-half to one hour.

Acute exposure will occur only (1) by accident, such as equipment failure, and (2) if workers enter enclosures or tanks without proper precautions. (See 6.8 Tank and Equipment Cleaning and Repairs.)

8.1.5.2 *Chronic Poisoning.* Chronic poisoning results from continued or frequently repeated exposure to relatively low concentrations of carbon disulfide. It probably occurs only from inhalation of vapor and is insidious in development. The most serious forms result in acute mental disturbance, or in severe injury to the nervous system.

8.1.6 *TOXIC EFFECTS FROM EXTERNAL CONTACT.* Carbon disulfide dissolves fat and can remove it from the skin, causing dryness and cracking, and producing sites of entry for harmful bacteria. Contact with the skin may cause only a temporary reddening and a burning sensation. If the liquid is not allowed to escape by evaporation, there may be extreme pain almost immediately, and later a more or less severe chemical burn.

8.1.7 *TOXIC EFFECTS AFTER ORAL INTAKE.* Poisoning by drinking carbon disulfide is rare. The signs are: loss of consciousness; pallor of the face, with blueness (cyanosis) of the lips; widening of the pupils; a rapid, feeble pulse: shivering; convulsious. If the quantity swallowed is not a fatal one, consciousness returns rapidly, but fatigue, dizziness and headache may last for days. Small quantities by mouth may cause vomiting, diarrhea and headache.

8.2 Prevention and Control

8.2.1 *VENTILATION.* The most important factor in prevention of posioning is ventilation adequate to keep the atmospheric concentration of carbon disulfide within a safe limit. Ventilation should aim at maintaining a concentration not exceeding 15 ppm by volume. See 6.1.1.

8.2.2 *EMPLOYEE EDUCATION.* (See 6.4 Employee Education and Training.) Employees should be instructed to eat a diet adequate in vitamins (especially B and C vitamins) as well as in carbohydrates, fats, proteins and minerals; to spend as much time as possible in the fresh air when climate is favorable, and to obtain adequate sleep. They should report to the Medical Department any signs of substandard physical condition.

8.2.3 *PREPLACEMENT PHYSICAL EXAMINATION.* Careful preplacement examinations should be made on all men who are to work with carbon disulfide. Certain individuals, who might be susceptible to the action of carbon disulfide, should not be assigned to operations using it. Exposure should be absolutely prohibited to:

(a) alcoholics,

(b) those with a history of gastro-intestinal disorders, abnormal blood pressure (high or low), peripheral vascular diseases or neurological diseases of any type.

(c) those with a history of abnormal behavior or impaired mentality.

8.2.4 *PERIODIC PHYSICAL EXAMINATIONS*

Workers exposed to carbon disulfide should be examined frequently, preferably every 3 or 4 weeks, by a physician acquainted with the hazards involved. The periodic examination should include standardized measurements of blood pressure, simple observations of the reflexes, and queries as to the symptoms listed in 8.1.3. The occurrence of abnormal blood pressure readings or reflexes, or of the symptoms of chronic carbon disulfide poisoning should lead at once to examination of the place of work, the manner in which the affected man performs his work, and his medical condition as compared with fellow workers in the same occupational group. Consideration should be given to at least temporary removal to work free from exposure to carbon disulfide.

A rotating schedule should be set up for workers exposed to carbon disulfide so that periods of exposure are followed by periods, at least as long, of work in uncontaminated air.

8.3 Personal Protective Equipment

8.3.1 *GENERAL.* Personal protective equipment is not an adequate substitute for safe working conditions and carefulness on the part of individual employees. Furthermore, if personal protective equipment is to be used effectively, each worker must be fully informed with respect to its proper employment, and trained in its use.

8.3.2 *RESPIRATORY EQUIPMENT.* All respiratory equipment should be approved by the United States Bureau of Mines for the use to which it is to be put and should be used in strict compliance with the instructions issued by the manufacturer.

8.3.2.1 *Low Concentrations of Vapor; Brief Exposure.* Suitable respiratory protection is needed if even small concentrations of carbon disulfide vapor are to be encountered. For concentrations of vapor not exceeding 2 per cent by volume, and for relatively brief exposure periods, an industrial gas mask with full face mask and canister, approved by the United States Bureau of Mines, may be used, provided also that the oxygen content of the air is not less than 16 per cent by volume. Such respirators should be readily available at all points where such limited exposures occur. They are not suitable for emergency, since, in emergency, the actual carbon disulfide concentration is unknown.

8.3.2.2 *High Concentrations of Vapor; Prolonged Exposure; Emergencies*
Where the vapor concentration exceeds 2 per cent by volume, or is unknown, as in most emergency situations, or when the oxygen content of the atmosphere is below 16 per cent by volume, or when exposure is prolonged, supplied-air respiratory equipment of appropriate design with full face masks, should be used by all persons entering the contaminated area. This is true also for oxygen-deficient atmospheres, such as those which exist frequently in storage tanks, tank cars, pits, and sewers handling carbon disulfide waste.

Such supplied-air respiratory equipment consists of approved types of:

(a) hose masks, with or without air pump, as may be required to maintain an adequate air supply (hose inlet must be in a vapor-free atmosphere),

(b) air line masks with compressed air supply, equipped with a suitable filter and a proper reducing valve or other device designed to effect delivery of air to the face piece under optimum pressure.

> NOTE: Hose or air line masks are suitable for use only where conditions will permit safe escape in case of failure of the air supply.

(c) self-contained breathing apparatus with proper reducing valve and filter, containing an adequate supply of stored oxygen or air (such equipment allows greater mobility but usually requires more training for its proper employment).

8.3.2.3 *Inspections.* Gas masks and other respiratory protective equipment should be inspected at regular intervals and should be cleaned and serviced after each use. It is particularly important that canisters and oxygen cylinders be replaced before they become exhausted.

8.3.3 *RESCUE HARNESS.* A safety belt and life line should be used in every case where the wearer of respiratory equipment enters a confined, irrespirable atmosphere. (See 6.8 Tank and Equipment Cleaning and Repairs.) A man should be stationed outside the contaminated area to act in case of an emergency; this attendant should also be provided with adequate protective equipment in case it becomes necessary for him to enter the contaminated area.

8.3.4 *SKIN PROTECTION.* To prevent injury to the hands of workers exposed to liquid carbon disulfide or to carbon disulfide solutions, gloves used should be impervious to this chemical product. If rubber gloves are a necessity, the ones selected should have the greatest resistance to carbon disulfide. The hands should be coated with a salve,* and a thin cotton glove worn directly over this salve and beneath the rubber gloves. Gloves should be washed daily. Rubber gloves should be washed inside and out, and thoroughly aired and dried to remove the carbon disulfide.

8.4 First Aid and Medical Treatment

8.4.1 *GENERAL PRINCIPLES*

8.4.1.1 First aid comprises simple measures which can be taken to make the patient comfortable and conserve his life.

8.4.1.2 Remove the patient to fresh air or to a well-ventilated room. If respiration has stopped, start artificial respiration at once by the prone pressure or the Eve rocking method.

8.4.1.3 Keep the patient quiet and comfortably warm, but not hot.

8.4.1.4 Call a physician immediately.

Do not give anything by mouth to an unconscious patient.

8.4.2 *SPECIFIC ACTIONS*

8.4.2.1 *Acute Poisoning by Inhalation.* Remove promptly from the contaminated atmosphere. If breathing has stopped, give artificial respiration by the prone pressure or the Eve rocking method. If oxygen is available and one familiar with oxygen inhalation apparatus is present, give oxygen. Attempts to give oxygen by one not familiar with the apparatus may cause loss of valuable time or actually harm the patient. Keep the patient comfortably warm. Call a physician as soon as possible.

8.4.2.2 *Chronic Poisoning.* Chronic poisoning may produce sudden hysteria or violent behavior. If necessary, tie the patient's arms and legs to prevent him from injuring himself and others. Call a physician at once. A patient suffering from psychic disturbance due to carbon disulfide should always be hospitalized.

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* An excellent salve for this purpose is an emulsion of fats sold by Duke Laboratories, Inc., 375 Fairfield Avenue, Stamford, Connecticut, under the name, "Eucerin".

8.4.2.3 *Skin Contact.* Remove contaminated clothing and do not allow patient to wear it until it is thoroughly aired and free from carbon disulfide. Wash skin thoroughly with plenty of water.

8.4.2.4 *Contact with Eyes.* If liquid carbon disulfide is splashed into the eyes, they should be washed promptly, for at least 15 minutes, with copious quantities of water. Medical attention should be obtained.

8.4.2.5 *Taken Internally.* If a worker has swallowed carbon disulfide and is conscious, he should be made to vomit by drinking a glassful of lukewarm salty water, or soapy warm water. If necessary, the patient should be encouraged to stick his finger down his throat to produce vomiting. Repeat this procedure at least three times. Call a physician promptly.

The medical information in this publication has been supplied by the Medical Advisory Committee of the Manufacturing Chemists' Association.

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Chapter 7

Hydrocarbon Solvents

The commercially available hydrocarbons find their principal utilization as solvents and thinners. They may be classed in two broad groups, depending on whether they are derived from petroleum or from coal tar. Those from petroleum, or the so-called straight-run naphthas, are conveniently sub-divided into the following classes:

(a) *Aliphatic naphthas:* the most commonly used naphthas, solvents, and diluents, such as mineral spirits and V. M. & P. naphtha.

(b) *Naphthenic naphthas:* "semi-high solvency" naphthas made from segregated crude oils.

(c) *High-solvency naphthas:* selective extracted fractions of naturally high-aromaticity distillates.

(d) *Close-cut naphthas:* superfractionated, almost chemically pure materials such as hexane, heptane, cyclopentane and methylcyclopentane.

The coal-tar hydrocarbons include not only products obtainable as such, from coal tar, *i.e.*, benzene and toluene, but also solvents prepared from coal-tar materials by such simple chemical reactions as hydrogenation or alkylation. Examples of solvents in the latter category are "Decalin" and "Tetralin." The coal-tar solvent naphthas are mixtures of higher-boiling aromatic hydrocarbons. They are available in several grades of which two are most common: light solvent naphtha, distilling between 130 and 160° C. and high-flash solvent naphtha, distilling between 150 and 200° C.

The monocyclic and bicyclic terpene hydrocarbon solvents offered by the pine-tree processing industry are a third important member of this group.

Petroleum Solvents

The petroleum-derived solvents were originally used in the paint and varnish industry because of their cheapness, but the old straight-run distillation methods of producing solvents are no longer equal to what is demanded of new solvents. As a consequence, new processes have been introduced, such as catalytic cracking, selective solvent extraction, hydrogenation, polymerization and alkylation. These have yielded petroleum solvents which are specially tailored to fit the needs of many industries. Now petroleum fractions are available which possess any of the following characteristics: a narrow boiling range, stability, an evaporation rate that

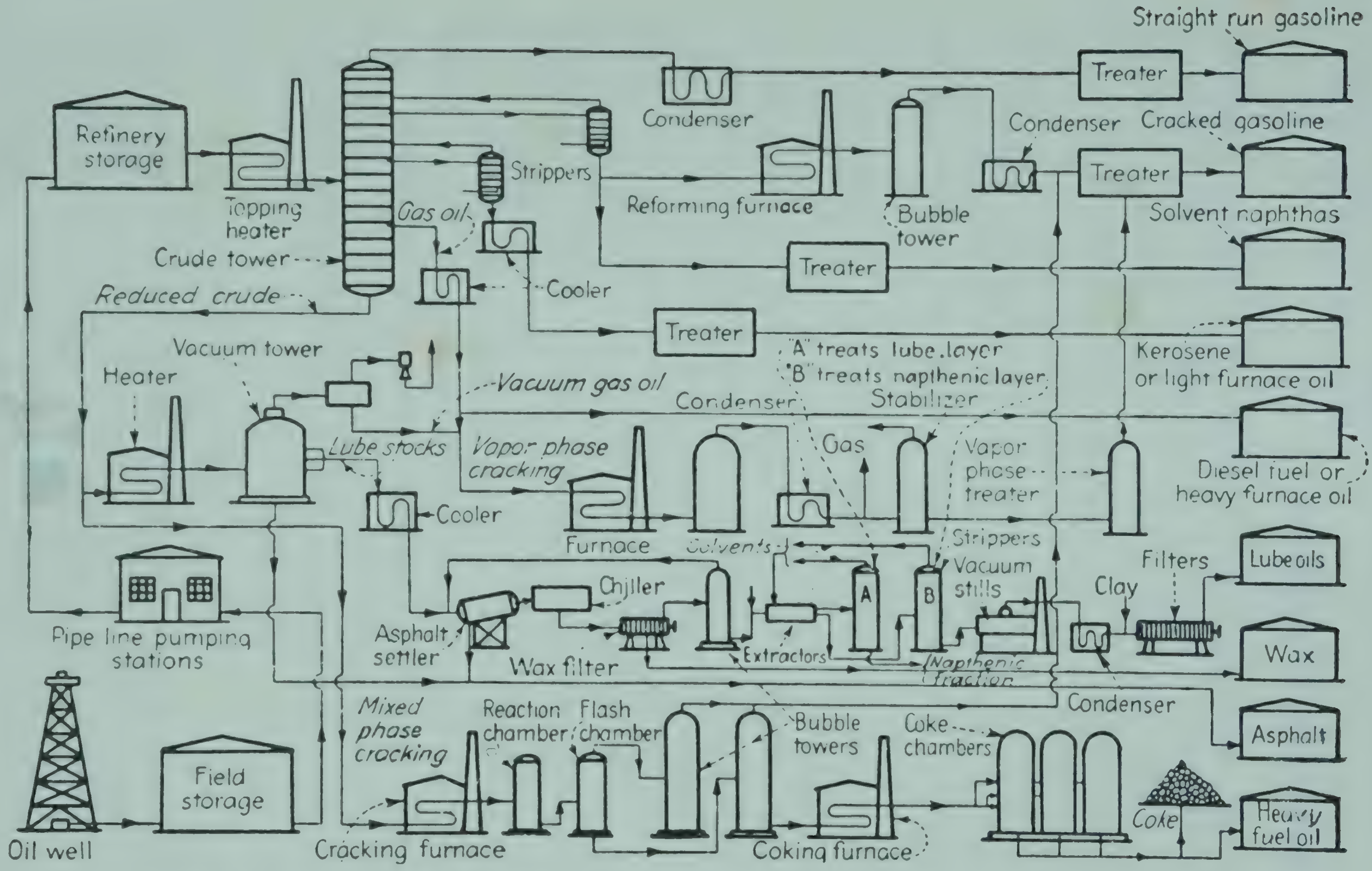

Straight run gasoline
Refinery storage
Topping heater
Crude tower
Reduced crude
Gas oil
Strippers
Cooler
Condenser
Reforming furnace
Bubble tower
Treater
Condenser
Cracked gasoline
Treater
Solvent naphthas
Treater
Treater
Kerosene or light furnace oil
"A" treats lube layer
"B" treats napthenic layer
Condenser
Stabilizer
Vacuum tower
Heater
Vacuum gas oil
Lube stocks
Vapor phase cracking
Gas
Vapor phase treater
Diesel fuel or heavy furnace oil
Cooler
Furnace
Solvents
Strippers
Vacuum stills
A
B
Filters
Lube oils
Clay
Pipe line pumping stations
Asphalt settler
Chiller
Wax filter
Extractors
Napthenic fraction
Wax
Condenser
Mixed phase cracking
Reaction chamber
Flash chamber
Bubble towers
Coke chambers
Asphalt
Oil well
Field storage
Cracking furnace
Coking furnace
Coke
Heavy fuel oil

Figure 7.1. Generalized Over-all Flow Sheet from Oil Well to Salable Products.[1]

Average yield of principal petroleum products in gallons from 1 bbl. (42 gal.) crude charged during 1940 (from "Petroleum Facts and Figures, 1941") was

Gasoline	18.4
Kerosene	2.4
Lubricants	1.2
Gas oil & distillates	6.0
Residual fuel oil	10.2
Total	38.2

Total operating cost in cents per bbl. of charging stock. (From U.S. Tariff Commission Report, 1932, on Costs of Refining Petroleum Products)

Operating labor	5.37
Fuel	4.52
Chemicals	4.82
Repairs, maintenance	3.66
Other direct	10.50
O'head, ins., deprec.	13.95
Total	42.82

meets special requirements, and suitable solvent power. These fractions are known in certain industries as either solvents or diluents, and they are called by such names as mineral spirits, V. M. & P. naphtha, Stoddard solvent, lacquer diluent, insecticide base, benzene substitute, toluene substitute and by many trade-mark designations.

From the standpoint of structure, solvents made from hydrocarbons can be conveniently divided into five groups: (1) the paraffins, or alkanes, having the general formula C_nH_{2n+2}; these occur as liquids and solids with the exception of the lower members, which exist as gases. (2) The cycloparaffin or cycloalkane group has the general formula C_nH_{2n} and is a closed chain or ring-like in structure. (3) The olefin (alkene or ethylene) hydrocarbons have the general formula C_nH_{2n} and are characterized by an ethylene linkage or double bond. The diolefin compounds may have a chain structure and are then known as alkadienes; or they may have a ring structure, in which case they are known as cyclodienes. (4) The last group comprises the aromatic compounds characterized by the presence of a benzene-type ring.

A procedure[3] has been worked out for classifying hydrocarbons that is based on their miscibility with nitromethane, aniline and benzyl alcohol, as well as on such constants as melting point, boiling point, density and the degree of unsaturation, determined by bromide-bromate titration. The solubilities of a number of hydrocarbons in nitromethane are plotted in Fig. 7.2 (page 242).

Lipkin and Kurtz[4] have worked out an equation for calculating the molecular volume of saturated hydrocarbons:

$$V = 16.29\, n_1 + 13.15\, n_2 + 9.7\, n_3 + 31.2$$

where V = molecular volume, cc/gram mole at 20° C.
n_1 = number of chain carbon atoms
n_2 = number of ring carbon atoms
n_3 = number of ring junction carbon atoms
31.2 = residual volume constant

"Molecular volumes calculated by this equation are usually accurate within 1 cc per gram mole for mixtures of isomers. Individual compounds of the simpler structural types seldom deviate by more than 4 cc per gram mole. The data for dicyclic naphthenes show an average deviation of about 3 cc per gram mole, which for these compounds is 1 per cent.

"In terms of density the accuracy is usually within ±0.005, except for the first few members of any homologous series. The deviations are not systematic, however.

"In the case of normal paraffins, the volume increment for the CH_2 group has been shown independently by Calingaert and by Huggins not to become constant until high molecular weights are reached. A table of

TABLE 7.1. TYPICAL SPECIFICATIONS FOR ALIPHATIC AND NAPHTHENIC PETROLEUM SOLVENTS

Solvent No.[a]	1	2	3	4	5	6	7	8	9	10	11	12	13	14
A. P. I. gravity	70.5	70–73	64.0	62.0	62.0	55–61	55–60	45–53	47–54	41–43	46–51	50.0	43–48	43.0
Sp. gravity	0.7005	0.69–0.70	0.7238	0.7313	0.7313	0.73–0.75	0.74–0.76	0.77–0.80	0.76–0.79	0.81–0.82	0.77–0.79	0.7796	0.78–0.81	0.8109
Pounds/gal.	5.831	5.7–5.8	6.025	6.087	6.087	6.1–6.3	6.1–6.3	6.4–6.7	6.3–6.6	6.7–6.8	6.4–6.6	6.49	6.5–6.7	6.752
A. S. T. M. distillation, °F														
Initial B. P.	140	105	170	205	200	215–230	205–210	290	305	310	325	360	340–370	370
50% over	175	175–185	200	210	220	250	255–265	305	345	340	350	380	390–410	430
90% over	195	220	220	220	240	270	310–315	315–330	370	370	370	400	425–435	475
Dry point	205	245–260	235	232	260	295	365–370	325–345	395	395	395	405	455	505
End point	210	250–265	240	235	265	295–305	370–375	330–350	400	400	400	410	460	510
Kauri butanol[b]	33.5	34.0	37.5	38.0	38.0	35–39	35–39	36–47	31–40	42–46	34–36	31.0	29–37	32.0
Aniline point[c]	135	135	128	125	125	125–135	125–135	110–135	125–150	114–120	140	151	135–160	150
Nitrocellulose diln. ratio[d]	1.30	. . .	1.35	1.40	1.40	1.30	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .
Flash point[e], °F	. . .	. . .	. . .	. . .	. . .	. . .	. . .	85	103	105	115	141	130–150	150

[a] Material key:

1 = light lacquer diluent, benzene replacement
2 = rubber solvent
3 = intermediate lacquer diluent
4 = special extraction solvent
5 = heavy lacquer diluent, toluene replacement
6 = V. M. & P. (close cut)
7 = V. M. & P. (long cut)
8 = xylene replacement
9 = mineral spirits
10 = naphthenic mineral spirits
11 = high-flash mineral spirits
12 = high-flash (140°F.) dry cleaning solvent and paint thinner
13 = flat-finish thinner
14 = slow-dry thinner

[b] Using Stewart Research Lab. standardized and certified Kauri butanol solution.

[c] Equal volume method, A. S. T. M. D611-41T.

[d] At 10% final concentration.

[e] Tag closed cup method, A. S. T. M. D56-36.

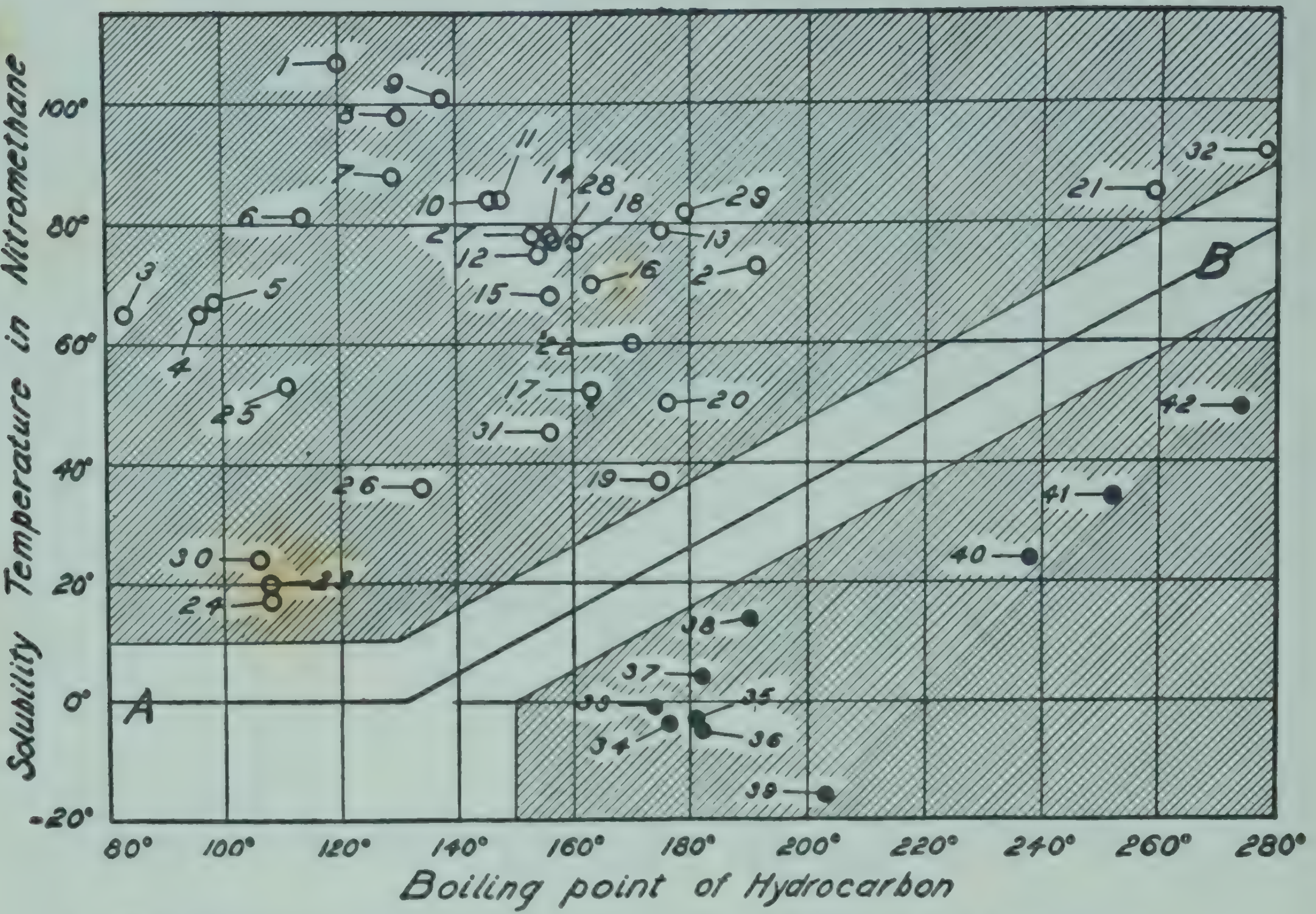
TABLE 7.2. TYPICAL PHYSICAL DATA ON ALIPHATIC SOLVENTS[2]

	"ESSO" HEXANE	"ESSO" HEPTANE	"ESSO" OCTANE	SOLVENT #1	SOLVENT #5	ESSO V. M. & P.	"VARSOL" #1	"VARSOL" #2
Boiling Range Code Number	1517	2022	2324	1325	1630	2529	3139	3141
Specific Gravity 60/60° F	.7074	.7290	.7271	.7005	.7202	.7335	.7839	.8035
Lbs/Gallon 60° F	5.89	6.07	6.05	5.83	5.98	6.11	6.53	6.69
Gravity—API 60/60° F	68.5	62.6	63.1	70.5	65.4	61.4	49.0	44.6
Flash ° F (Tag closed cup)	Below 0	22	45	Below 0	5	55	110	112
Distillation ASTM (D268)								
Initial Boiling Point ° F	154	207	230	130	160	250	315	324
10%	156	208	233	152	182	256	334	330
50	157	210	235	169	216	261	342	338
90%	158	212	239	207	269	272	367	367
Dry Point ° F	161	214	242	248	289	290	387	387
Final Boiling Point ° F	—	—	—	255	300	—	392	392
Viscosity, cp. at 25° C	0.374	0.495	0.518	0.389	0.462	0.575	0.918	0.898
K-B Value (Toluol = 100)	37	36	32	32	33	32	36	43
Aniline Point ° F	119	131	149	135	137	150	134	110
Approximate Composition (Philadelphia Club Method)								
% Aromatics	7.5	3.1	2.2	1.2	3.6	1.7	15	30.4
% Paraffins	75.4	63.0	68.0	81.0	76.2	83.1	42.5	35.2
% Naphthenes	17.1	33.9	29.8	17.8	20.2	15.2	42.5	34.4

TABLE 7.3. PHYSICAL CHARACTERISTICS OF "APCO" NAPHTHAS

	"RUB-SOL"	"PETROLENE"	"TROLUOIL"	"APCOLENE"	"DRYOLENE"	"APCOTHINNER"
A. P. I. Gravity	74.5	70.5	59.5	60.0	57.4	55.0
Specific gravity	0.687	0.700	0.740	0.738	0.749	0.758
Weight per gallon	5.72	5.85	6.15	6.10	6.23	6.30
A. S. T. M. Distillation						
IBP	98° F	140° F	200° F	204° F	209° F	240° F
5%	120	150	206	208	214	246
10%	130	153	208	210	218	248
20%	140	156	210	212	220	250
30%	148	159	212	215	224	252
40%	154	162	214	217	228	256
50%	160	165	217	220	232	260
60%	164	168	220	222	236	262
70%	168	172	225	225	240	264
80%	176	178	228	227	248	268
90%	186	188	236	234	258	276
95%	198	196	246	240	275	282
Dry point	202	201	250	246	279	288
Flash point	−40° F	−16° F	25° F	24° F	32° F	52° F
Spot dry time relation (C. P. Ethyl Ether = 1.0)	1.4	1.8	4.0	3.8	5.6	7.0
Kauri butanol value		32.7	38.5			39.0
Lacquer dilution value		15.1	14.8			13.8
Vapor pressure at 100° F (lbs. per sq. inch)	9.60	4.52	1.32	1.30	0.90	0.52

	"STOD-SOL"	#10 MINERAL SPIRITS	"APCO" 125	"APCO" 140	"APCO" 467	KEROSENE
A. P. I. Gravity	51.0	50.0	49.0	46.5	44.0	43.0
Specific gravity	0.775	0.779	0.783	0.794	0.806	0.810
Weight per gallon	6.46	6.50	6.55	6.60	6.75	6.75
A. S. T. M. Distillation						
IBP	308° F	306° F	325° F	368° F	396° F	379° F
5%	315	314	333	373	410	420
10%	318	317	336	375	412	428
20%	320	320	340	377	414	434
30%	325	324	344	380	419	440
40%	329	328	348	381	422	443
50%	331	331	352	383	427	446
60%	335	336	356	385	431	452
70%	340	341	362	388	436	459
80%	345	348	368	392	442	466
90%	358	360	378	396	452	479
95%	368	370	386	399	460	490
Dry point	380	381	392	406	467	498
Flash point	108° F	106° F	118° F	142° F	186° F	145° F
Spot dry time relation (C.P. Ethyl Ether = 1.0)	54.0	55.0	60.0	90.0	425.0	600.0
Kauri butanol value		34.0	33.5	32.0	29.5	29.5
Lacquer dilution value						
Vapor pressure at 100° F (lb. per sq. inch)	0.13	0.12	0.07	0.010	0.004	0.010



1. Dimethylcyclohexane
2. *tert*-Amylcyclohexane
3. 2,4-Dimethyl-2-pentene
4. 3-Heptene
5. 2-Heptene
6. 4-Methyl-2-heptene
7. 4,5,5-Trimethyl-2-hexene
8. 4,6-Dimethyl-2-heptene
9. 4-Methyl-2-octene
10. 1-Nonene
11. 4-Nonene
12. 1-Cyclohexyl-2-propene
13. *d*-Menthene
14. *d*-α-Pinene
15. *l*-α-Pinene
16. *l*-β-Pinene
17. Sabinene
18. Camphene
19. Phellandrene
20. *d*-Limonene
21. Caryophyllene
22. Dicyclopentadiene
23. 2,2-Dimethyl-3,4-hexadiene
24. 2,4-Heptadiene
25. 4-Methyl-1,5-heptadiene
26. 2,4-Octadiene
27. 4,5-Dimethyl-2,6-octadiene
28. 4-Propyl-1,5-heptadiene
29. 4-Allyl-2-octene
30. 3-Heptine
31. 4-Nonine
32. 1-Hexadecine
33. *sec*-Butylbenzene
34. *p*-Cymene
35. *m*-Diethylbenzene
36. *p*-Diethylbenzene
37. *n*-Butylbenzene
38. *tert*-Amylbenzene
39. Tetrahydronaphthalene
40. Phenylcyclohexane
41. 2,4-Dimethyl-3-benzylidenepentane
42. 2-Phenyl-3-isopropyl-4-methyl-2-pentene

Boiling points at atmospheric pressure for 32, 41, and 42 are estimated.

Figure 7.2. Solubility of Hydrocarbons in Nitromethane.[3] Temperature in °C. ○ Nonaromatic ● Aromatic

corrections to apply to the 16.28 cc term for paraffins has been given. All the available evidence indicates that these corrections are not needed for average paraffins or for the side chains of naphthenes.

"There is an appreciable difference in density between naphthenes of the same molecular weight and number of rings per molecule, depending on whether the rings are of the 5-carbon or 6-carbon types.

"The number of carbon atoms in naphthene rings can be calculated if the density, molecular weight, and number of rings per molecule are accurately known.

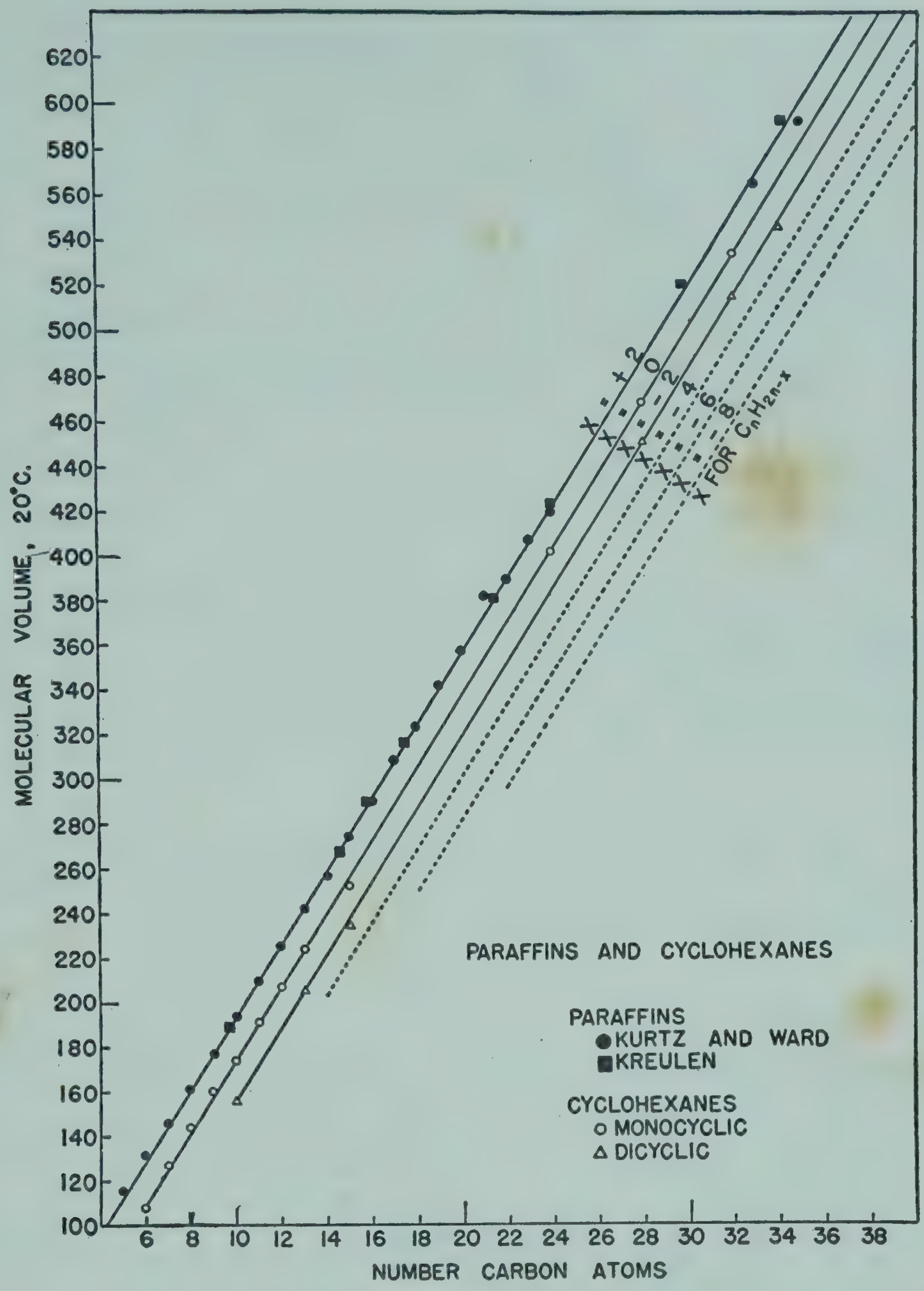


Figure 7.3. Linear Relation between Molecular Volume and Number of Carbon Atoms.[4]

"The cross-section of the normal CH_2 chain is 21.1 square angstroms, and this value is in good agreement with data on molecular dimensions calculated from other physical measurements.

"In order that the density of naphthenes could be calculated from data for the corresponding olefins or aromatics, the volume change on hydrogenation was obtained. Hydrogenation of an olefinic double bond increases molecular volume 6.2 cc on the average. Hydrogenation of an aromatic double bond increases the molecular volume 6.8 cc on the average.

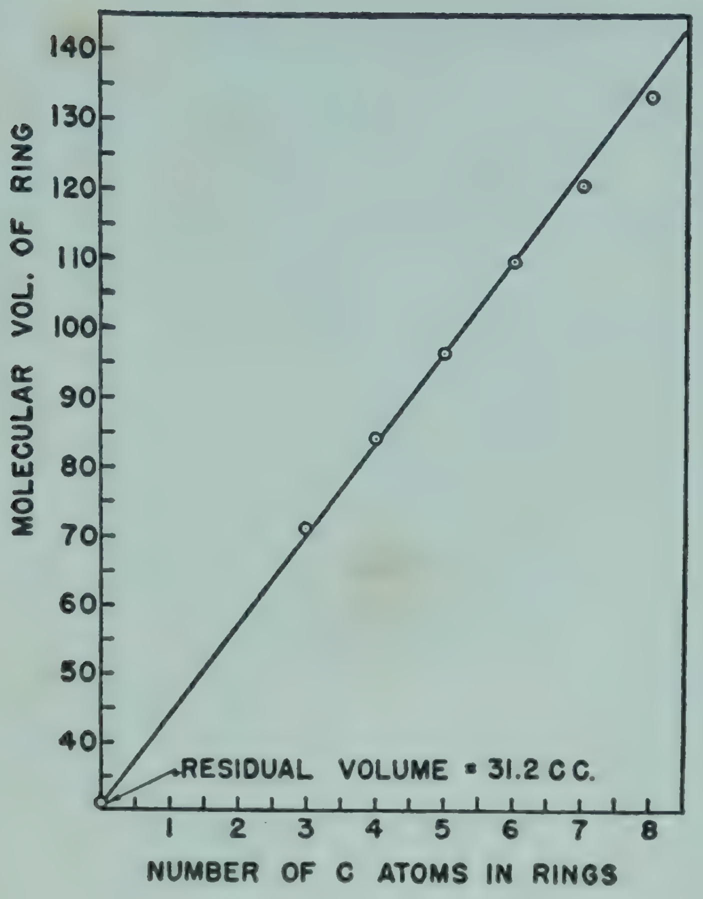


Figure 7.4. Linear Relation between Molecular Volume of Rings and Number of Carbon Atoms in Rings.[4]

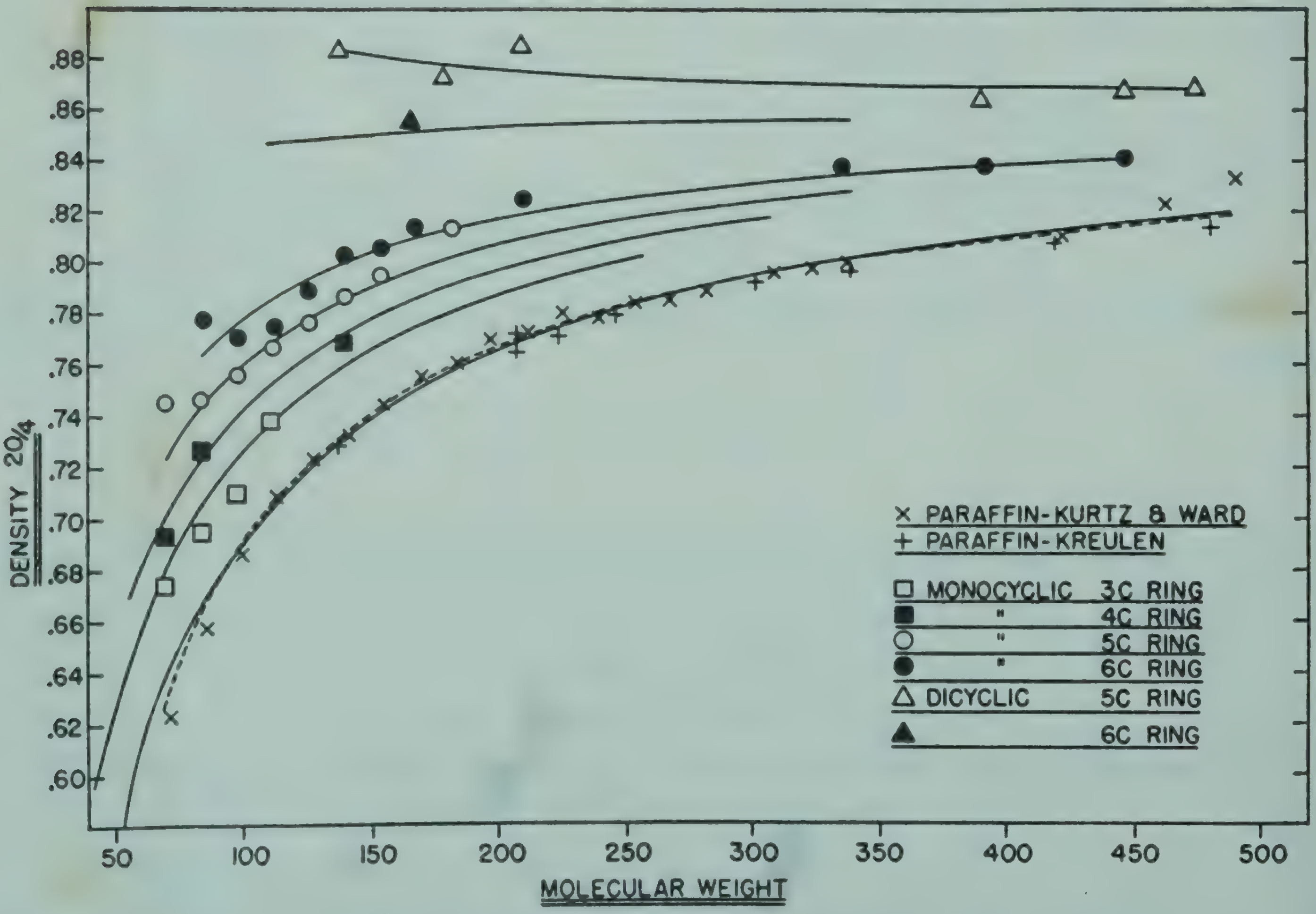


Figure 7.5. Agreement between Calculated and Experimental Densities.[4]

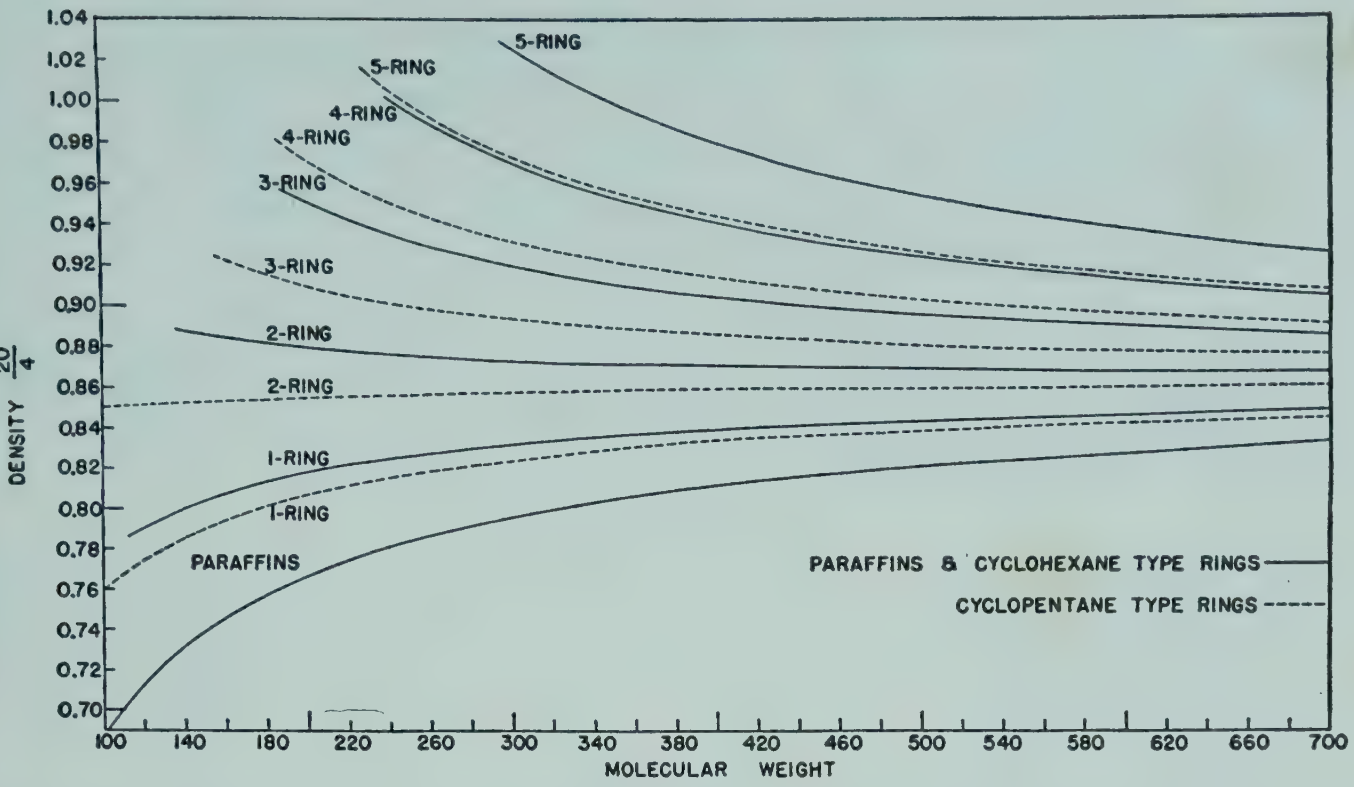


Figure 7.6. Density vs. Molecular Weight for Paraffins and Naphthenes of Cyclopentane and Cyclohexane Types.[4]

"The percentage of uncondensed ring CH_2 groups can be calculated in hydrocarbons of over 3000 molecular weight from the density. By this method Staudinger's hydrocyclorubber contains 60–62 ring CH_2 groups and 38–40 per cent chain CH_2 groups."

Petroleum Ether. Petroleum ether (benzinum, light ligroin, benzine) is a colorless liquid consisting mainly of hexane. It is soluble in alcohol, ether, chloroform, benzene, and fixed volatile oils. It will dissolve some types of cellulose ethers, oils, waxes and soft resins. Several grades of petroleum ethers meeting A. S. T. M. specifications are available; they are made by the fractionation of natural gasoline and are widely used as solvents.

	Grades		
Distillation range	I	II	III
Initial boiling point	80° F	95° F	136° F
10% evaporated	82	96	140
50% evaporated	83	97	144
90% evaporated	84	98	149
Dry point	86	99	151
Specific gravity at 60/60° F.	0.63	0.63	0.67
Vapor pressure at 70° F	12.1	8.3	5.1 psi abs
100° F.	20.5	15.0	9.5 psi abs
130° F.	33.5	25.0	16.6 psi abs
Weight per gallon at 60° F	5.3 lb.	5.3 lb.	5.6 lb.

Petroleum Naphtha. Several petroleum naphthas meeting A. S. T. M. specifications for precipitation naphtha and for dilution naphtha are available commercially. Their typical properties are as follows:

PRECIPITATION NAPHTHA

Distillation range	
Initial boiling point	126° F
10% evaporated	144
50% evaporated	167
90% evaporated	206
End point	234
Specific gravity at 60/60° F	0.692 to 0.702
Aniline point	58 to 60° C
Weight per gallon at 60° F	5.79 lbs.

DILUTION NAPHTHA

Distillation range	
Initial boiling point	194° F
5% evaporated	206
10% evaporated	208
50% evaporated	223
90% evaporated	245
95% evaporated	252
Dry point	258
Specific gravity at 60/60° F	0.734
Vapor pressure at 70° F	2.4 psi abs
100	3.1 psi abs
130	5.7 psi abs
Weight per gallon at 60° F	6.11 lbs.

Gasoline. Gasoline (petrol, motor spirits, petroleum ether, benzine, benzoline) is a colorless, highly volatile, flammable liquid of characteristic odor. It is obtained both from natural gas and from petroleum distillates. It is composed chiefly of hexanes and heptanes with smaller quantities of pentanes and octanes.

Boiling range	60–120° C
Freezing point	−90.6 to −95.4°C
Specific gravity	0.66–0.684
Refractive index	1.375–1.3877
Flash point	−50 to −10°F

Petroleum spirit. Petroleum spirit (ligroin, benzoline, benzine, petroleum ether, petroleum naphtha) is a colorless, flammable liquid composed, in the main, of hexanes and heptanes, with small amounts of octanes. It is soluble in alcohol, benzene, chloroform, ether, etc. It may be used as a solvent in paint and varnish manufacture, in rubber cement, an oil-cloth fabrication. It also finds application as a general solvent, in the extraction of oils, fats and greases, in detergent soaps, and as a detergent and degreasant for textiles, machines and hides.

Boiling range	80–130° C
Specific gravity	0.730 at 15° C
Refractive index	1.407–1.425

V. M. & P. Naphtha. Varnish Makers' and Painters' Naphtha as a solvent stands between gasoline and mineral spirit. Its solvency may be accentuated by the addition of coal-tar solvents or turpentine. It is used in paints and varnishes for dipping and spraying purposes, and its presence in these preparations imparts depth and gloss to the films. It is also used in short-oil fossil-gum varnishes, asphalt varnish, gloss furniture varnish, barrel paint, metalware enamels, penetrating stains, prepared waxes, metal and furniture polish, oil-type graining compounds and primers.

Boiling range	205–375° F
Specific gravity	0.73–0.76
Refractive index	1.41
Flash point	20–50° F

Mineral Spirits. Mineral spirits (petroleum distillate, oleum, heavy naphtha, turpentine substitute) is a colorless petroleum liquid of a sweet, pleasant odor. Because it has a high flash point and evaporates at about 31° C, it is used as a solvent and thinner in the paint and varnish industry, occupying the position long held by turpentine. Mineral spirits is used in brushing preparations where its rate of evaporation does not retard drying but permits easy working qualities and good flow. Its presence in the vehicle and thinner of mill whites, flat whites, undercoats and primers causes better dispersion of the pigments. It is used to replace turpentine entirely in oleoresinous products and, in a limited way, in short-oil fossil-gum varnishes and in solutions of blown oils. Pine oil, wood turpentine and dipentene are used with mineral spirits to mask its petroleum characteristic, to increase solvency and to impart flowing qualities. Mineral spirits will dissolve linoleate driers but will not hold them in solution permanently without the addition of an oil, higher fatty acid, or rosin.

Boiling range	305–400° F
Flash point	103° F
Specific gravity	0.76–0.79
Refractive index	1.42

Kerosene. Kerosene (coal oil, astral oil), an important petroleum distillate, is a mixture of hydrocarbons, boiling between 150 and 250° C. Because of its slow-drying properties kerosene imparts to paint and varnish mixtures good flow, penetration, easy brushing and working qualities, and prevents surface skinning. It is used in slow-drying paints, dipping primers, enamels, baking Japans, alkyd-resin varnishes, asphalt coatings and plastic and liquid cements. Kerosene also finds application as a thinner in dammar enamels and in cork-sticking lacquers; admixed with creosote it is used in shingle stains.

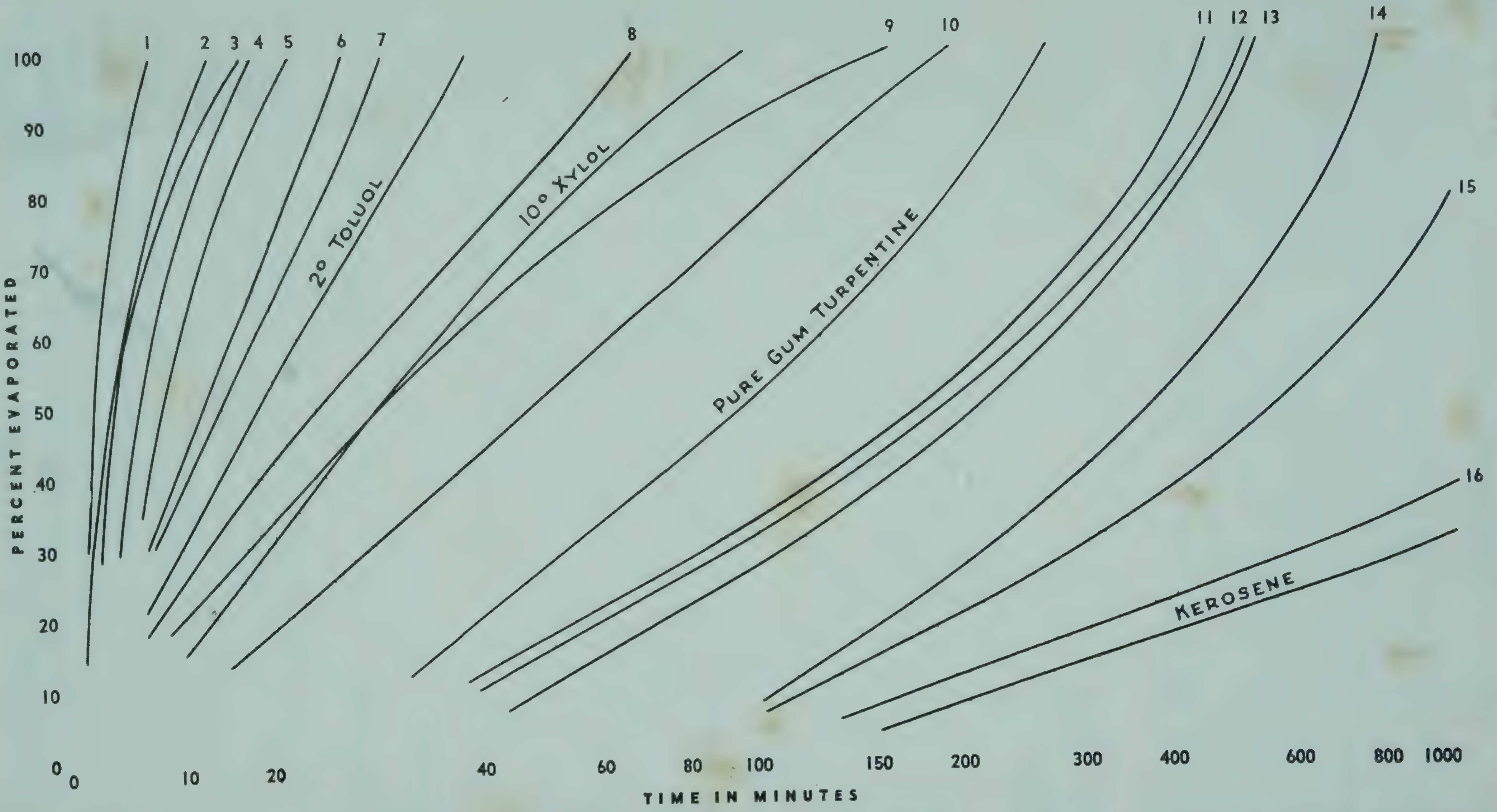


Figure 7.7. Evaporation Rates of Various Solvents and "Amsco" Petroleum Solvents. (Refer to key on opposite page.) 1-gram samples on "Amsco" Evaporometer.

Key to Figure 7.7.

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
A.P.I. Gravity—60° F.	75.5	70.5	70-73	64.0	64.0	62.0	62.0	55-61	55-60	45-53	47-54	41-43	46-51	50.0	43-48	43.0	Meets Federal Commercial Standard CS3-40
Specific Gravity—60° F.	.6836	.7005	.69-.70	.7238	.7238	.7313	.7313	.73-.75	.74-.76	.77-.80	.76-.79	.81-.82	.77-.79	.7796	.78-.81	.8109	
Pounds per Gal.—60° F.	5.690	5.831	5.7-5.8	6.025	6.025	6.087	6.087	6.1-6.3	6.1-6.3	6.4-6.7	6.3-6.6	6.7-6.8	6.4-6.6	6.49	6.5-6.7	6.752	
A.S.T.M. Distillation																	
I.B.P. °F.	145	140	105	195	170	205	200	215-230	205-210	290	305	310	325	360	340-370	370	
50%	150	175	175-185	200	200	210	220	250	255-265	305	345	340	350	380	390-410	430	340
90%	155	195	220	210	220	220	240	270	310-315	315-330	370	370	370	400	425-435	475	370
Dry Point	159	205	245-260	213	235	232	260	295	365-370	325-345	395	395	395	405	455	505	395
End Point	160	210	250-265	215	240	235	265	295-305	370-375	330-350	400	400	400	410	460	510	400
Ⓐ Kauri Butanol	30.5	33.5	34.0	35.5	37.5	38.0	38.0	35-39	35-39	36-47	31-40	42-46	34-36	31.0	29-37	32.0	—
Ⓑ Aniline Point	145	135	135	135	128	125	125	125-135	125-135	110-135	125-150	114-120	140	151	135-160	150	—
Ⓒ Nitrocellulose Dilution Ratio	1.25	1.30	—	1.30	1.35	1.40	1.40	1.30	—	—	—	—	—	—	—	—	—
Ⓓ Flash Point °F	*In addition to these tests all products are better than water white, pass full corrosion test, are color stable, good odored and doctor sweet.*									85	103	105	115	141	130-150	150	104

MATERIAL KEY

1—AMSCO Hexane
2—AMSCO Textile Spirits
3—AMSCO Rubber Solvent
4—AMSCO Heptane
5—AMSCO Special Textile Spirits
6—AMSCO Special Extraction Solvent
7—AMSCO Lactol Spirits
8—AMSCO Special Naphtholite
9—AMSCO Naphtholite
10—AMSCO Naphthol Mineral Spirits
11—AMSCO Mineral Spirits
12—AMSCO 46 Spirits
13—AMSCO Hi Flash Mineral Spirits
14—AMSCO Light Retardsol
15—AMSCO No. 460 Solvent
16—AMSCO Retardsol
17—AMSCO Stoddard Solvent

Note: Where a spread is shown in tests—materials of several specifications are available.

NOTES ON TESTS

Ⓐ Using Stewart Research Laboratory Standardized and Certified K. B. Solution.

Ⓑ Equal volume method, ASTM D611-41T.

Ⓒ At 10% Final Concentration with Butyl Acetate.

Ⓓ Tag Closed Cup Method, D56-36.

Distillation range	345–525° F
Specific gravity	0.798
Refractive index	1.45
Flash point	1.50° F

High-Solvency Petroleum Naphthas. These aromatic petroleum solvents are, in a sense, products of conversion. Their principal sources today are (1) Edeleanu extracts of distillates of highly aromatic crude oils, and (2) products of catalytic cracking under certain conditions. General specifications on the available aromatic petroleum solvents are listed in Table 7.4.

TABLE 7.4. TYPICAL SPECIFICATIONS[6]

Solvent No.[a]	A	B	C	D	E	F
A. P. I. gravity	40.0–47.0	41.0	33.0–37.0	33.0	28.0	28.0–32.0
Sp. gravity	0.825–0.793	0.8203	0.860–0.840	0.8602	0.8871	0.887–0.865
Pounds/gal.	6.87–6.60	6.830	7.16–6.99	7.163	7.387	7.38–7.20
A. S. T. M. distillation, °F.						
Initial B. P.	200–210	240	275–285	305	350	340–360
50% over	235–240	275	295–315	355	405	375–385
90% over	260–265	300	330–340	395	435	395–405
Dry point	270–275	330	350–360	410	460	405–410
End point	275–280	335	360–370	415	465	410–415
Kauri butanol[b]	63.0–80.0	74.0	75–90	75.0	75.0	75–85
Aniline point, ° F.	20–50	15	0–20	20	20	10–20
Mixed aniline point[c], ° F.	80–100	85	60–80	88	88	75–85
Nitrocellulose diln. ratio (10% final concn. with butyl acetate)	1.90–2.30	2.15	...	...	...	...
Per cent aromatics[d]	45.0–65	62.0	70–85	...	...	...

[a] Material key:

A = toluene replacement
B = light xylene replacement
C = heavy xylene replacement
D = Mineral spirits replacement
E = Medium boiling solvent
F = High boiling solvent

[b] Using Stewart Research Lab. standardized and certified Kauri butanol solution.

[c] Mixed aniline cloud point is run with 5.0 cc. of solvent, 5.0 cc. of mineral spirits of 140° F aniline cloud point, and 10.0 cc. of freshly distilled C. P. aniline.

[d] Philadelphia Paint & Varnish Production Club method.

"Solvesso"[2] is a trade mark for a group of hydrogenated petroleum naphthas. By the process of hydrogenation such physical changes are produced as increase in Kauri-butanol values and in the aniline points. Their solvency is in direct relationship to the boiling range; that is, the higher the boiling point the higher the solvent power. This explains why the higher fractions, such as the residual hydrogenated naphthas, have a solvent power superior to that of the lighter fractions. These compounds are ex-

TABLE 7.5. Typical Physical Data on Aromatic Solvents[2]
(ESSO Standard Oil Company)

	"SOLVESSO" TOLUOL	"SOLVESSO" XYOL	"SOLVESSO" #100	"SOLVESSO" #150	HEAVY AROMATIC NAPHTHA
Specific gravity at 60/60° F	0.8686	0.8707	0.8749	0.8919	0.9244
Lbs/gallon, 60° F	7.23	7.25	7.29	7.42	7.70
Gravity—API 60/60° F	31.4	31.0	30.2	27.2	21.6
Flash, °F (tag closed cup)	46	80 Min.	100 Min.	150 Min.	140
Distillation ASTM (D268)					
Initial boiling point °F	227	275	306	375	313
10%	231	279	311	380	346
50%	231	282	317	387	404
90%	232	284	327	392	482
Dry point °F	233	287	343	398	524
Final boiling point °F	—	—	—	410	526
Viscosity, cp. at 25° C	0.572	0.641	0.797	1.193	1.480
K-B value (toluol = 100)	100	93	90	83	85
K-B value (after 75% is evaporated)	100	—	98	114	—
Mixed aniline point °C	10.0	10.6	12.0	20.1	24.9
Per cent aromatics	99.5	99.5	99.5	95	83 (Min.)

With the exception of HEAVY AROMATIC NAPHTHA and "SOLVESSO" 150 these products are +25 Saybolt color or better, and pass doctor and corrosion tests. Color of "SOLVESSO" 150 is +21 Saybolt or better. HEAVY AROMATIC NAPHTHA is dark-colored and not fully refined.

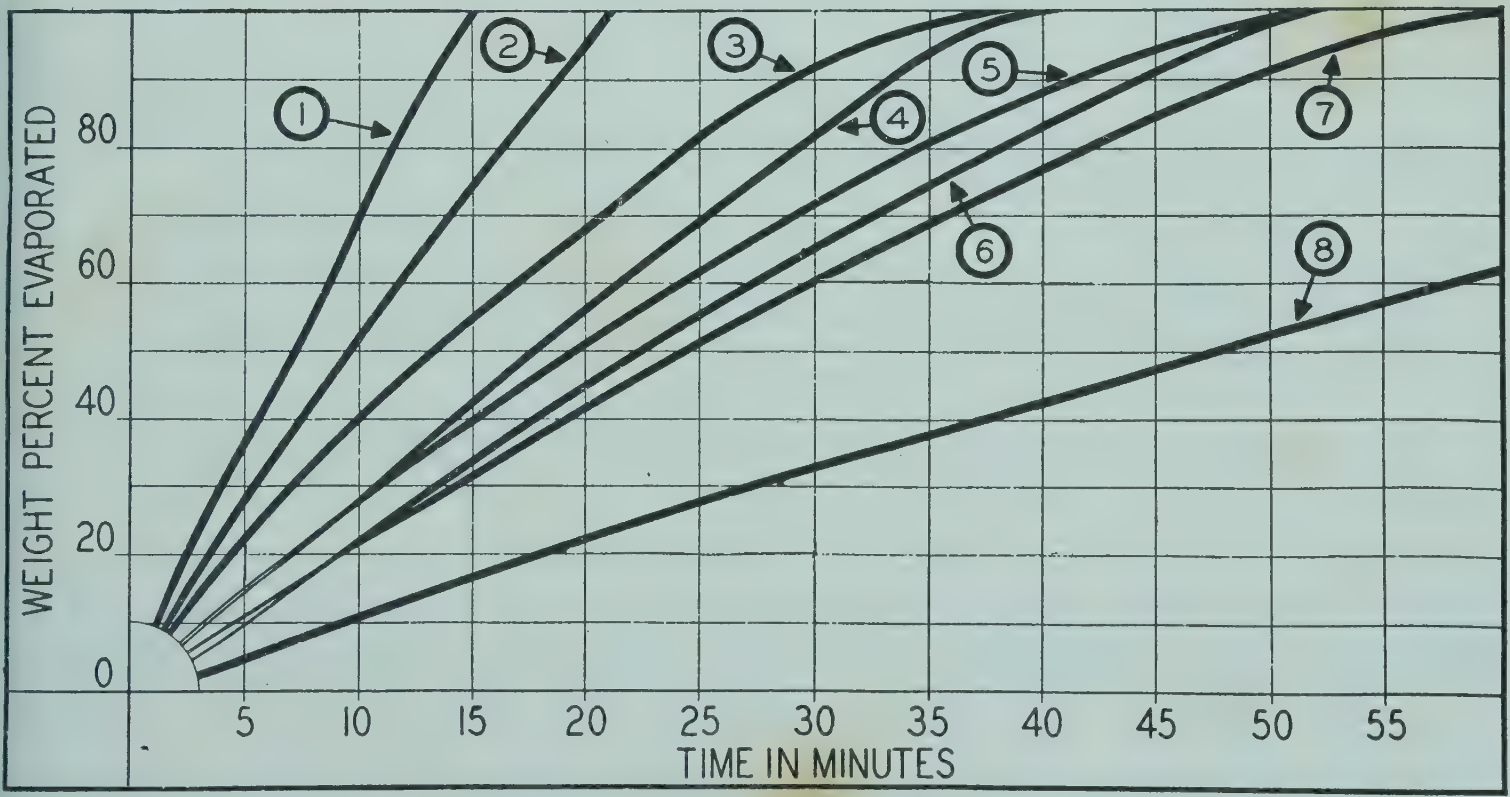


Figure 7.8. Rapidly Evaporating Solvents.[2]

1. "Esso" Hexane 1517
2. "Old Esso" Solvent #3, 1421
3. "Old Esso" Solvent #4, 1724
4. "Esso" Heptane 2022
5. "Old Esso" Solv. #6, 2027
6. "Solvesso" Toluol 2300
7. "Esso" Octane 2324
8. "Solvesso" Xylol 2829

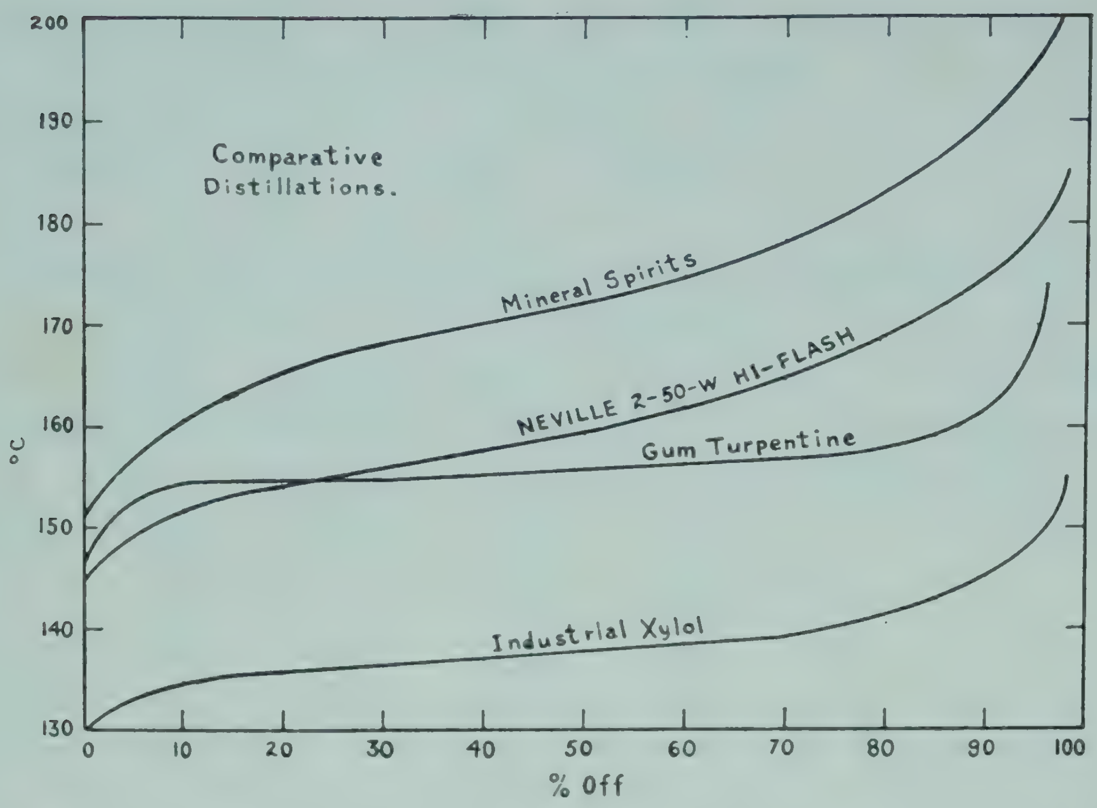


Figure 7.9. Effect of Temperature in Comparative Distillation of Various Solvents.[22]

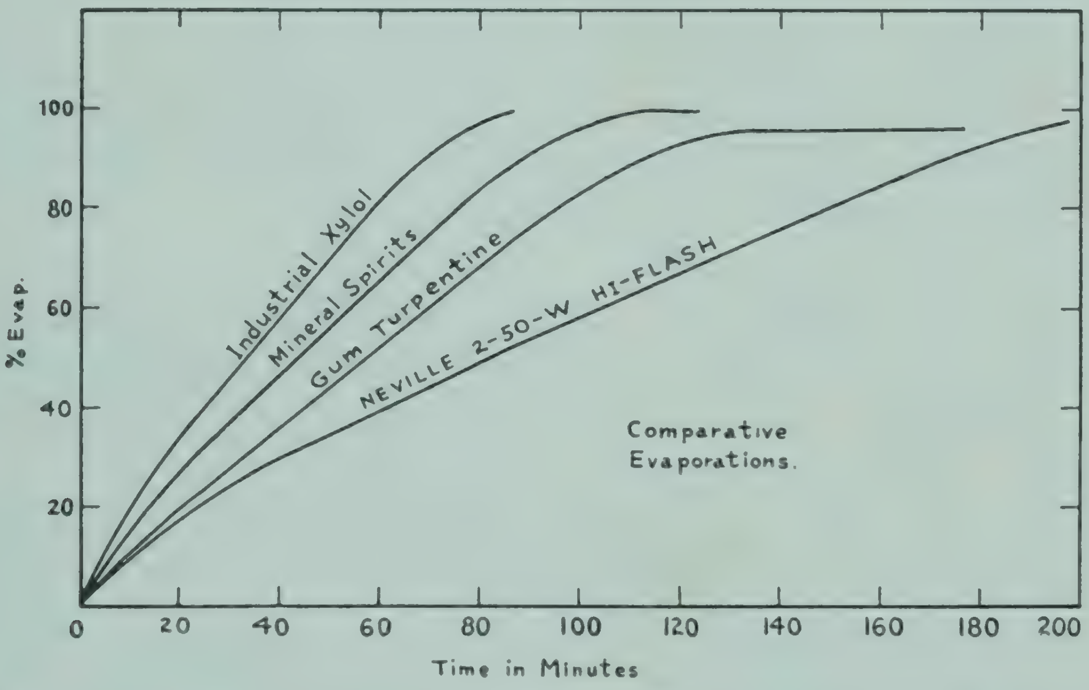


Figure 7.10. Evaporation Rate of Solvents in Fig. 7.9 at 25°C.

cellent solvents for resins, especially the synthetic type. They are used as solvents in such protective coatings as alkyd-resin finishes, phenol-resin varnishes, short-oil fossil-gum varnishes, primers and dipping enamels where their presence prevents skinning and gelling. They form constant-minimum boiling mixtures with methyl and ethyl alcohol, acetone, ethyl formate, methyl acetate, isopropyl alcohol, methyl ethyl ketone, *tert.*-butyl alcohol and ethyl ether. Physical data on "Solvesso" and related solvents is presented in Table 7.6.

TABLE 7.6. TYPICAL SPECIFICATIONS: CLOSE-CUT PETROLEUM NAPHTHAS[6]

Solvent No.[a]	1	2	3	4	5	6
Mol. wt.	86.10	...	100.20	...	70.13	84.16
Sp. gravity	0.668	0.668	0.691	0.724	0.739	0.748
Boiling range, ° F.	155.3–156.3	152–157	208.6–209.6	198–210	120.2–121.2	160.7–161.7
Vapor pressure at 100° F., lb./sq. in. abs.	...	4.9	...	...	...	...

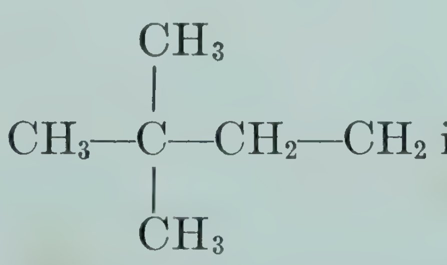
[a] Material key:
1 = technical *n*-hexane
2 = commercial *n*-hexane
3 = technical *n*-heptane
4 = commercial heptane
5 = technical cyclopentane
6 = technical methylcyclopentane

SATURATED HYDROCARBONS

Butanes

n-Butane ($CH_3—CH_2—CH_2—CH_3$). *n*-Butane is a colorless, flammable gas of high calorific content. The technical grade, which is a fraction of natural gasoline, contains about 96% *n*-butane and about 4% isobutane. It is used in low-boiling extractions of vegetable oils and animal fats.

Boiling range	27 to 32° F
Specific gravity of vapor at 0° C and 760 mm. Hg (Air = 100)	2.06
Liquid at 60/60° F	0.582
Vapor pressure at 70° F	32.0 psi abs
105	57.5 psi abs
130	83.0 psi abs
Weight per gallon at 60° F	4.86 lbs.

2,2-Dimethylbutane (Neohexane) 
$CH_3—\underset{CH_3}{\overset{CH_3}{C}}—CH_2—CH_2$ is a water-white liquid available as a pure grade containing 99% 2,2-dimethylbutane and small proportions of cyclopentane and alkenes, and a technical grade made up of about 90% neohexane, 5% cyclopentane, 4% *n*-pentane and 1% olefins. It is used as a low-boiling solvent.

2,2-Dimethylbutane (99%)

Boiling point	49.5° C
Critical temperature	212.0° C
Melting point	98.0° C
Specific gravity at 20/4° C	0.649
Refractive index at 20° C	1.369
Weight per gallon at 60° F	5.45 lbs.

2,2-Dimethylbutane (90%)

Boiling range	120.9 to 122.9° F
Density of liquid at 60° F	5.47 lb. per gal.
Distillation range	
Initial boiling point	121° F
5% evaporated	122
10% evaporated	122
50% evaporated	123
90% evaporated	126
95% evaporated	127
Dry point	132
Specific gravity at 60/60° F	0.655 to 0.661
Refractive index at 20° C	1.3725
Sulfur content, maximum	0.05%
Vapor pressure at 70° F	5.7 psi abs
100	10.4 psi abs
130	18.1 psi abs

Pentanes

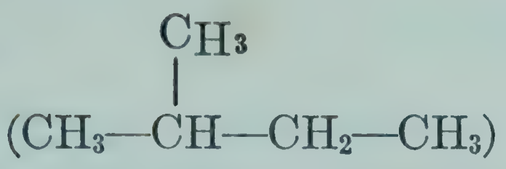
***n*-Pentane** ($CH_3—CH_2—CH_2—CH_2—CH_3$). *n*-Pentane is a colorless liquid obtained from natural gasoline; it is a 99% pure product containing about 0.5% isopentane and is available commercially. There is also a technical grade that contains 90% *n*-pentane and about 8% isopentane. It is a low-boiling solvent and is a basic raw material in the manufacture of amyl compounds.

n-Pentane (90%)

Boiling range	94 to 100° F
Specific gravity at 60/60° F	0.630
Vapor pressure	16 psi abs
Weight per gallon at 60° F	5.24 lbs.

n-Pentane (99%)

Boiling point	36.0° C
Critical temperature	197.0° C (386.6° F)
Critical pressure	33 atm ++(485 psi abs.)
Melting point	−130° C
Refractive index at 20° C	1.358
Specific gravity at 20/4° C	0.626
Weight per gallon at 60° F	5.26 lbs.



Isopentane ($CH_3{-}\overset{\displaystyle CH_3}{\overset{|}{C}}H{-}CH_2{-}CH_3$) is a colorless liquid obtained from natural gasoline. The refined commercial product contains about 99% isopentane and less than 1% *n*-pentane. The technical grade contains about 90% isopentane with about 9% *n*-pentane and small quantities of *n*-butane. It is used mainly for extraction where a low-boiling agent is needed.

Isopentane (Technical)

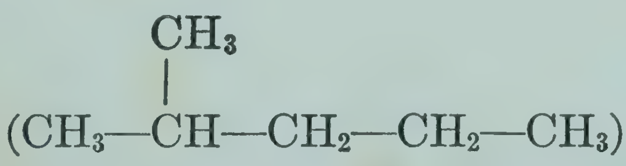
Distillation range	
Initial boiling point	80° F
10% evaporated	82
50% evaporated	83
90% evaporated	84
Dry Point	86
Molecular weight	72.14
Purity	90%
Specific gravity at 60/60° F	0.626 (0.624)
Vapor pressure at 70° F	12.6 psi abs
100	20.7 psi abs
130	34.0 psi abs
Weight per gallon at 60° F	5.21 lbs.

Isopentane (99%)

Boiling point	28.0° (82.4° F)
Critical temperature	190° C
Density of liquid at 60° F	5.20 lb. per gal.
Critical pressure	32.9 atm. (484 psi)
Melting point	−159° C
Specific gravity at 20/4° C	0.619
Refractive index at 20° C	1.355

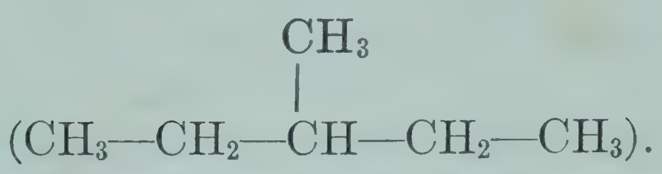
Cyclopentane ($CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2$). The commercial product is composed of 95% cyclopentane with paraffinic hydrocarbons as the principal impurity.

Boiling range	120.2 to 121.2° F
Specific gravity at 60/60° F	0.739
Refractive index at 20° C	1.4030
Weight per gallon	6.15 lbs.



2-Methylpentane ($CH_3{-}\overset{\displaystyle CH_3}{\overset{|}{C}}H{-}CH_2{-}CH_2{-}CH_3$) is a colorless liquid. The technical grade contains about 5% of impurities, most of which is 3-methylpentane. It is a low-boiling solvent.

Boiling range	139.9 to 140.0° F
Specific gravity at 60/60° F	0.658
Refractive index at 20° C	1.3718
Weight per gallon at 60° F	5.48 lbs.



3-Methylpentane ($CH_3{-}CH_2{-}\overset{\overset{\textstyle CH_3}{|}}{CH}{-}CH_2{-}CH_3$). The technical grade has a purity of 95% with small amounts of *n*-hexane and 2-methylpentane as impurities.

Boiling range	145.3 to 146.3° F
Specific gravity at 60/60° F	0.668
Refractive index at 20° C	1.3762
Weight per gallon at 60° F	5.56 lbs.

Methyl Cyclopentane [$CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH(CH_3)$]. The technical grade has a purity of 95% and contains 3% *n*-hexane.

Boiling range	160.7 to 161.7° F
Specific gravity at 60/60° F	0.748
Molecular weight	84.16
Refractive index at 20° C	1.4082
Weight per gallon	6.23 lbs.

Hexanes

n-Hexane ($CH_3{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_3$) is a water-white liquid obtained from the lighter fractions of natural gasoline. There are several grades available of which one contains 95% *n*-hexane with about 4% methylcyclopentane; another is composed of 75% *n*-hexane with 25% methylcyclopentane; a third grade is a mixture of the isomeric hexanes. Normal hexane is one of the most useful solvents in the extraction industries. It contains an appreciable proportion of methylcyclopentane, to which may be attributed some of its unique solvent power. Normal hexane is especially adapted to the extraction of oils, fats and other materials from varied plant products such as alfalfa, castor beans, cocoa beans, corn, cotton seed, soybeans and animal products such as wool.

n-Hexane (75%)

Distillation range	
Initial boiling point	152° F
10% evaporated	154
50% evaporated	154
90% evaporated	155
Dry point	156
Specific gravity at 60/60° F	0.668
Vapor pressure at 70° F	3.1 psi abs
100	4.9 psi abs
130	8.7 psi abs
Weight per gallon at 60° F	5.56 lbs.

n-Hexane (95%)

Boiling range	155.3 to 156.3° F
Specific gravity at 60/60° F	0.668
Refractive index at 20° C	1.3767
Weight per gallon at 60° F	5.56 lbs.

n-Hexane (Isomeric Hexanes)

Distillation range	
Initial boiling point	135° F
10% evaporated	140
50% evaporated	144
90% evaporated	149
Dry point	151
Specific gravity at 60/60° F	0.669
Vapor pressure at 70°	4.7 psi abs
100	9.0 psi abs
130	16.3 psi abs
Weight per gallon at 60° F	5.57 lbs.

Isohexane. Commercial isohexane is essentially a mixture of 2-methylpentane and 3-methylpentane with small amounts of neohexane, methylcyclopentane and cyclopentane.

Distillation range	
Initial boiling point	133° F
10% evaporated	136
50% evaporated	139
90% evaporated	142
Dry point	144
Specific gravity at 60/60° F	0.668
Vapor pressure at 70°	3.7 psi abs
100	7.0 psi abs
130	13.0 psi abs
Weight per gallon	5.56 lbs.

Heptanes

***n*-Heptane** ($CH_3{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_3$). The commercial product is a colorless liquid of about 95 per cent purity with about 4 per cent methylcyclohexane. There is another grade which is a mixture of the isomeric heptanes.

In the extraction field, normal heptane is especially applicable to fat and oil extractions, such as the processing of castor beans, corn, cotton seed, sugar cane, garbage, and meat scraps.

It is widely used as a solvent in rubber processing and in the preparation of quick-drying rubber cements. It is also used in lacquers, paints, varnishes and quick-drying inks, and as a cleaning solvent in the printing trade.

n-Heptane (95%)

Boiling range	208.6 to 209.6° F
Distillation range	
Initial boiling point	201° F
10% evaporated	205
50% evaporated	206
90% evaporated	207
Dry point	207
Specific gravity at 60/60° F	0.691
60/60	0.709
Refractive index at 20° C	1.3894
Vapor pressure at 70° F	0.9 psi abs
100	1.6 psi abs
130	2.6 psi abs
Weight per gallon at 60° F	5.76 lbs.

n-Heptane (Mixed Isomers)

Distillation range	
Initial boiling point	168° F
10% evaporated	175
50% evaporated	180
90% evaporated	195
Dry point	200
Specific gravity at 60/60° F	0.724
Vapor pressure at 70° F	2.5 psi abs
100	5.0 psi abs
130	9.4 psi abs
Weight per gallon at 60° F	6.03 lbs.

Isooctane. Commercial isooctane is a mixture of highly branched octanes, as well as some hexanes, heptanes and nonanes. A mixed octane, essentially a mixture of isomeric octanes, is also available. These are used as solvents and thinners.

Isooctane (Technical Grade)

Distillation range	
Initial boiling point	164° F
10% evaporated	184
50% evaporated	205
90% evaporated	289
Dry point	338
Specific gravity at 60/60° F	0.725
Vapor pressure at 70° F	2.2 psi abs
100	2.9 psi abs
130	5.4 psi abs
Weight per gallon at 60° F	6.04 lbs.

Isooctane (Mixed Isomers)

Distillation range	
Initial boiling point	200° F
10% evaporated	213
50% evaporated	226
90% evaporated	245
Dry point	259
Specific gravity at 60/60° F	0.736
Vapor pressure at 70° F	2.4 psi abs
100	3.0 psi abs
130	5.4 psi abs
Weight per gallon at 60° F	6.13 lbs.

Isoheptane. Commercial isoheptane is for the most part comprised of isomeric branched chain heptanes. Appreciable quantities of cyclohexane, methylcyclohexane and dimethylcyclohexane are also present. In addition to its use in conventional petroleum naphtha and fuel applications, it is being applied in extraction and crystallization processes, in preparation of paints, varnishes, and lacquers, and as a cleaning agent.

Distillation range	
Initial boiling point	133° F
10% evaporated	136
50% evaporated	139
90% evaporated	142
Dry point	144
Specific gravity at 60/60° F	0.668
Vapor pressure at 70° F	3.7 psi abs
100	7.0 psi abs
130	13.0 psi abs
Weight per gallon at 60° F	5.56 lbs.

UNSATURATED HYDROCARBONS

Pentene-1 ($\mathrm{CH_2—CH—CH_2—CH_2—CH_3}$). The technical product is 95% pure with as much as 4% pentene-2. It also contains some paraffins.

Boiling range	85 to 87° F
Specific gravity at 60/60° F	0.644
Refractive index at 20° C	1.370
Weight per gallon at 60° F	5.36 lbs.

Pentene-2 ($\mathrm{CH_3—CH{=}CH—CH_2—CH_3}$). The technical product has a purity of 95% with about 4% of other olefinic and paraffinic hydrocarbons as impurities.

Boiling range	96 to 99° F
Specific gravity at 60/60° F	0.651
Refractive index at 20° C	1.3800
Weight per gallon at 60° F	5.42 lbs.

(Text continued on page 268)

TABLE 7.7. SOME OF THE PHYSICAL PROPERTIES[7] OF CERTAIN HYDROCARBONS

Paraffins

	B P °F	B P °C	SP GR D_4^{20}	SP GR D_{60}^{60}	°API	DENSITY AT 60°F LB/GAL	R I n_D^{20}	ANILINE POINT		FLASH POINT °F
								°F	°C	
Methane	−258.8	−161.5	—	—	—	—	—	—	—	—
Ethane	−127.4	−88.56	—	0.378	242.8	3.15	—	—	—	—
Propane	−44.1	−42.28	0.5034 Est.	0.509	146.5	4.239	@ −42.2 1.3395	—	—	−140 Est.
Isobutane	+10.3	−11.78	0.5588 Est.	0.564	119.4	4.697	@ −25° C. 1.3514	225.7	107.6	−117 Est.
Normal Butane	+30.9	−0.61	0.5788 Est.	0.584	110.8	4.864	@ −15° C. 1.3562	181.6	83.1	−103 Est.
2,2-Dimethyl propane	49.0	+9.45*	@ 0° C. 0.613	0.5969 Est.	106.5	2.972	@ 0° C. 1.3515	215.6 Est.	102.0 Est.	— —
Isopentane	82.3	+27.94	0.6191	0.624	95.3	5.197	1.3539	172.0	77.8	−68
Normal pentane	96.9	36.05	0.6263	0.6312	92.7	5.257	1.3577	159.3	70.7	−59
2,2-Dimethyl butane	121.9	49.72*	0.6494	0.6541	84.8	5.445	1.3691	177.8	81.0	−54
2,3-Dimethyl butane	136.5	58.05	0.6617	0.6654	81.2	5.537	1.3751	161.6	72.0	—
2-Methyl pentane	140.4	60.2	0.6532	0.6579	83.6	5.475	1.3715	166.5	74.7	—
3-Methyl pentane	145.8	63.2	0.6640	0.6687	80.1	5.566	1.3765	156.7	69.3	—

Normal hexane	155.8	68.8	0.6594	0.6641	81.6	5.526	1.3750	155.5	68.6	−18
2,2-Dimethyl pentane	174.7	79.3	0.6737	0.6783	77.1	5.646	1.3823	172.9	78.3	—
2,4-Dimethyl pentane	177.4	80.8	0.6729	0.6775	77.4	5.638	1.3824	173.8	78.8	—
2,2,3-Trimethyl butane	177.8	81.0	0.6901	0.6946	72.2	5.782	1.3895	162.3	72.4	—
3,3-Dimethyl pentane	186.8	86.0	0.6933	0.6978	71.3	5.808	1.3910	157.5	69.7	—
2,3-Dimethyl pentane	193.5	89.7	0.6952	0.6997	70.7	5.825	1.3920	154.6	68.1	—
2-Methyl hexane	194.2	90.1	0.6787	0.6833	75.2	5.687	1.3851	164.5	73.6	—
3-Methyl hexane	197.2	91.8	0.6900	0.6945	72.2	5.782	1.3887	158.9	70.5	—
3-Ethyl pentane	199.9	93.3	0.6986	0.7030	70.55	5.835	1.3937	151.3	66.3	—
Normal heptane	209.1	98.4	0.68375	0.68728	74.4	5.720	1.38774	158.0	70.0	+28
2,2,4-Trimethyl pentane (Isooctane)	210.7	99.3	0.69194	0.69640	71.7	5.796	1.39151	176.7	80.4	+16
2,2,3,3-Tetra methyl butane†	223.7	106.5	0.7167	0.7210	64.75	6.002	1.408	166.6	74.8	—
2,2-Dimethyl hexane	224.6	107.0	0.6956	0.7001	70.6	5.828	1.3931	172.4	Est. 78.0	—
2,5-Dimethyl hexane	228.7	109.3	0.6943	0.6988	71.0	5.817	1.3929	172.4	78.0	—
2,4-Dimethyl hexane	229.8	109.9	0.6993	0.7037	69.6	5.857	1.3958	164.1	73.4	—

TABLE 7.7. *Continued*

Paraffins

	B P °F	B P °C	SP GR D^{20}_{4}	SP GR D^{60}_{60}	°API	DENSITY AT 60°F LB/GAL	R I n^{20}_{D}	ANILINE POINT		FLASH POINT °F
								°F	°C	
2,2,3-Trimethyl pentane	230.2	110.1	0.7162	0.7205	64.9	5.997	1.4030	161.2	70.8	—
3,3-Dimethyl hexane	231.8	111.0	0.7086	0.7130	66.95	5.935	1.3993	161.6	72.0 Est.	—
2,3,4-Trimethyl pentane	235.4	113.0	0.7195	0.7238	64.0	6.025	1.4046	154.9	68.3	—
2-Methyl, 3-Ethyl pentane	237.2	114.0	0.7182	0.7225	64.35	6.014	1.4033	153.0	67.2	—
2,3,3-Trimethyl pentane	237.6	114.2	0.7258	0.7301	62.3	6.078	1.4075	152.6	67.0	—
2,3-Dimethyl hexane	240.3	115.7	0.7124	0.7168	65.9	5.967	1.4014	159.1	70.6	—
2-Methyl heptane	243.0	117.2	0.6978	0.7022	70.0	5.845	1.3947	165.2	74.0	—
3,4-Dimethyl hexane	244.0	117.8	0.7195	0.7238	64.0	6.025	1.4045	154.4	68.0	—
4-Methyl heptane	244.4	118.0	0.7163	0.7206	64.9	5.997	1.3981	160.9	71.6	—
3-Methyl, 3-Ethyl pentane	245.1	118.4	0.7274	0.7317	61.9	6.090	1.4079	150.6	65.9	—
3-Ethyl hexane	245.8	118.8	0.7122	0.7166	66.0	5.964	1.4020	155.7	68.7	—
3-Methyl heptane	246.4	119.1	0.7058	0.7102	67.7	5.913	1.3985	162.0	72.2	—
Normal octane	258.1	125.6	0.7028	0.7072	69.8	5.851	1.3977	161.8	72.1	63

Olefins

Ethylene	−154.7	−103.7	0.309 @ 4.4/4	—	—	—	—	—	—	—
Propylene	−53.7	−47.6	0.520	0.524	138.5	4.367	1.3625 @ −47.7	—	—	—
Isobutylene	+20.1	−6.6	0.596	0.601	103.9	5.013	1.3814 @ −25	58.8	14.9	—
Butene-1	+21.0	−6.1	0.595	0.600	104.3	5.001	1.3803	—	—	—
Butene-2 L.B.	33.8	+1.0	0.608	0.613	99.3	5.102	@ −25 —	—	—	—
Butene-2 H.B.	38.7	+3.7	0.608	0.613	99.3	5.102	—	—	—	—
3 Methyl butene 1	68.2	20.1	0.6284	0.6333	91.9	5.271	1.3653	—	—	—
Pentene-1	86.4	30.2	0.6410	0.6438	87.6	5.375	1.3710	66.7	19.3	—
Isopentene	88.0	31.1	0.6504	0.6551	84.5	5.453	1.3777	—	—	—
Pentene-2 L.B.	96.4	35.8	0.6482	0.6510	85.9	5.417	1.3790	64.4	18.0	—
Pentene-2 H.B.	98.6	37.0	0.6503	0.6550	84.5	5.453	1.3817	64.4	18.0	—
2-Methyl butene-2	101.1	38.4	0.6620	0.6667	80.7	5.550	1.3878	51.8	11.0	—

TABLE 7.7. *Continued*

Diolefins

	B P °F	B P °C	SP GR D^{20}_{4}	SP GR D^{60}_{60}	°API	DENSITY AT 60°F LB/GAL	R I n^{20}_{D}	ANILINE POINT		FLASH POINT °F
								°F	°C	
Propadiene	−29.7	−34.3	0.5966 Est.	0.6020	103.5	5.015	1.4169 @ −34.3	—	—	—
Butadiene-1,3	+23.5	−4.75	0.6222	0.6271 Est.	94.1	5.220	1.422 @ −6	—	—	—
Butadiene-1,2	+50.5	+10.3	0.676* 0° C.	—	—	—	1.4205 @ +1.3	—	—	—
Pentadiene-1,4	78.8	+26.0	0.6594	0.6553	94.4	5.455	1.3883	—	—	—
2-Methyl butadiene-1,3 (Isoprene)	93.3	34.076	0.6808	0.6767	77.6	5.632	1.42158	—	—	—
2-Methyl butadiene-1,2	104.9	40.5	0.6833	0.6766	77.6	5.632	1.4166	—	—	—
Pentadiene-1,3 (Mixed) (Piperylene)	108.5	42.5	0.684	0.689	73.9	5.734	1.4309	—	—	—
Pentadiene-1,2	112.5	44.7	0.6904	0.6966	71.6	5.799	1.4191	—	—	—
Pentadiene-2,3	120.2	49.0	0.7023	0.6980	71.2	5.811	—	—	—	—
Naphthenes										
Cyclopentane	120.7	49.3	0.7460	0.7502	57.1	6.246	1.4068	64.4	18.0	—
Methylcyclopentane	161.2	71.8	0.7488	0.7530	56.4	6.270	1.4098	95.0	35.0	—

1,1-Dimethyl cyclopentane	190.4	88.0	0.7523	0.7564	55.6	6.296	1.4126	11.30	45.0	—
1,3-Dimethyl · cyclopentane	195.3	90.7	0.7456	0.7498	57.2	6.243	1.4076	113.0	45.0	—
1,2-Dimethyl cyclopentane L.B.	197.24	91.8	0.7450	0.7492	57.4	6.236	1.416	118.4	48.0	—
1,2-Dimethyl cyclopentane H.B.	210.7	99.3	0.7723	0.7763	50.8	6.462	1.420	118.4	48.0	—
Ethyl cyclopentane	218.1	103.4	0.7657	0.7698	52.3	6.410	1.5197	101.7	38.7	—
1,2,3-Trimethyl cyclopentane	234.5	112.5	0.7588	0.7629	54.0	6.350	1.4259	105.8	41.0	—
1,2,4-Trimethyl cyclopentane	235.0	112.75	0.7565	0.7606	54.5	6.334	1.4156	—	—	—
1,1,3-Trimethyl cyclopentane	239.9	115.5	0.7703	0.7744	51.2	6.448	1.4223	—	—	—
1-Methyl, 3-ethyl cyclopentane	248.9	120.5	0.763	0.7671	53.0	6.385	1.4214	—	—	—
1-Methyl, 2-ethyl cyclopentane L.B.	249.8	121.0	0.7691	0.7732	51.5	6.437	1.4284	126.0	52.2	—
Isopropyl cyclopentane	263.3	128.5	0.7766	0.7806	49.8	6.398	1.4264	—	—	—
n-Propyl cyclopentane	268.5	131.4	0.7765	0.7805	49.8	6.498	1.4266	113.0	45.0	—
Cyclohexane	177.3	80.7	0.7781	0.7821	49.4	6.512	1.4263	87.8	31.0	—
Methyl cyclohexane	212.5	100.3	0.7692	0.7723	51.7	6.430	1.4230	105.8	41.0	—
1,1-Dimethyl cyclohexane	246.2	119.0	0.7810	0.7850	48.7	6.537	1.4293	120.2	49.0	—
1,4-Dimethyl cyclohexane L.B.	247.3	119.6	0.7626	0.7667	53.0	6.385	1.4224	118.4	48.0*	—

TABLE 7.7. *Continued*

Naphthenes (Continued)

	B P °F	B P °C	SP GR D^{20}_{4}	SP GR D^{10}_{60}	°API	DENSITY AT 60°F LB/GAL	R I n^{20}_{D}	ANILINE POINT		FLASH POINT °F
								°F	°C	
1,3-Dimethyl cyclohexane L.B.	248.7	120.4	0.7663	0.7704	52.2	6.413	1.425	122.0	50.0*	—
1,2-Dimethyl cyclohexane L.B.	254.7	123.7	0.776	0.7800	49.9	6.494	1.4303	107.6	42.0	—
1,4-Dimethyl cyclohexane H.B.	256.3	124.6	0.783	0.7870	48.3	6.552	1.426	118.4	48.0*	—
1,3-Dimethyl cyclohexane H.B.	256.8	124.9	0.783	0.7870	48.3	6.552	1.426	122.0	50.0*	—
1,2-Dimethyl cyclohexane H.B.	266.0	130.0	0.7965	0.8004	45.3	6.660	1.433	107.6	42.0*	52
Ethyl cyclohexane	269.2	131.8	0.7878	0.7918	47.2	6.592	1.4329	111.2	44.0	—
Isopropyl cyclohexane	310.1	154.5	0.799	0.8029	44.7	6.686	1.441	122.0	50.0	—
n-Propyl cyclohexane	310.5	154.7	0.7932	0.7971	46.0	6.637	1.4371	122.0	50.0	—

Aromatics

Benzene	176.2	80.1	0.87896	0.8742	30.4	7.278	1.50123	−34	−30	10
Toluene	231.2	110.68	0.86697	0.8629	32.5	7.184	1.49685	−34	−30	50
Ethyl benzene	277.1	136.15	0.86690	0.8630	32.5	7.184	1.49587	−34	−30	60
p-Xylene	281.1	138.4	0.86100	0.8571	33.6	7.137	1.49615	—	—	—
m-Xylene	282.7	139.3	0.8641	0.8603	33.0	7.163	1.49741	—	—	—
o-Xylene	291.3	144.05	0.88011	0.8863	28.2	7.378	1.50547	−4	−20	70
Isopropyl benzene	306.5	152.5	0.8620	0.8583	33.4	7.145	1.4922	5	−15	126
n-Propyl benzene	319.0	159.45	0.8621	0.8582	33.4	7.145	1.4922	−34	−30	87

* Value of doubtful accuracy.

† MP 104° C or 219.2° F.

Mixed Pentenes (C_5H_{10}). The commercial product is a water-white liquid containing about equal parts of trimethylethylene and pentene-2, with small proportions of other isomers. It is insoluble in water but soluble in methyl alcohol, ethyl ether, ethyl acetate, acetone, aromatic and aliphatic hydrocarbons, fixed oils, mineral oil, oleic and stearic acids, and hot paraffin and carnauba waxes, the latter two congealing when cool.

Distillation range	
Initial boiling point	Not below 32° C
Not less than 90%	Below 45° C
Final boiling point	Not above 60° C
Pentane content	Less than 5.0%
Specific gravity at 20° C	0.66
Weight per gallon	5.50 lbs.
Color	Water-white

Isoheptene. Commercial isoheptene contains about 85% branched heptenes.

Distillation range	
Initial boiling point	172° F
10% evaporated	182
50% evaporated	195
90% evaporated	205
Dry point	209
Specific gravity at 60/60° F	0.712
Vapor pressure at 70° F	2.2 psi abs
100	4.0 psi abs
130	6.5 psi abs
Weight per gallon at 60° F	5.93 lbs.

Isooctenes. The commercial product contains about 85% of branched octenes.

Distillation range	
Initial boiling points	175° F
10% evaporated	185
50% evaporated	209
90% evaporated	292
Dry point	340
Specific gravity at 60/60° F	0.722
Vapor pressure at 70° F	2.2 psi abs
100	3.0 psi abs
130	5.4 psi abs
Weight per gallon at 60° F	6.01 lbs.

Coal-Tar Solvents

The coal-tar solvents include cyclohexane, solvent naphthas, tetrahydronaphthalene, decahydronaphthalene, methylnaphthalene, and dimethylnaphthalene. They have well-defined boiling points, uniform evaporation rates, good solvency, mild odor, and excellent ability to disperse and wet certain pigments. Cuts can be made to give either quick or slow drying rates without residue. These solvents are miscible with anhydrous alcohols, petroleum hydrocarbons, esters, and many of the common organic solvents.

As a result of studies[8] made on aluminum paint, it was found that the coal-tar solvents have superior leafing properties because of their comparatively high surface tensions.

Naphthas. "Naphtha" is an old term referring to the volatile portion of the *bitumen liquidum candidum* described by Pliny. Milton mentions in the second book of "Paradise Lost" that naphtha and asphalt were used to illuminate the palace of Pandemonium in the lower world. The word was used by the alchemists to characterize any volatile, mobile and flammable liquid. Today it has a more scientific meaning. The lighter fractions of naphthas are composed of mixtures of toluene, xylene isomers, ethyl benzene and propyl benzene; and the heavier mixtures are made up of pseudocumene, isodurene, mesitylene, ethyl-*p*-xylene, hemimellitene, indene, durene, coumarone and naphthalene hydrocarbons.

The heavy naphthas (crude heavy solvent naphtha) of commerce are sold as "refined" and "semi-refined" grades, of which there are a number of fractions. Their solvent power is the same as that of the light grades but they differ in that their higher boiling points and lower evaporation rates make them unsuitable for lacquer compositions. The following is an approximate analysis of heavy solvent naphthas.

	% by wt.
Coumarone, indene, styrene, etc	30
High-flash naphtha components	50
Methyl naphthalene and naphthalene	20

The dark grades are used as solvents in dark-colored paints, pipe coatings, shingle stains, ship-bottom paints, bituminous paints and enamels, and asphalt road-tars; they are also used to saturate asbestos board, brake lining, and fabric transmission felt.

High-flash naphtha (sold under the trade mark "Hi-Flash") is a solvent for oils and natural and synthetic resins. This fraction of naphtha is also used as a slow-drying solvent and thinner in varnishes, paints, enamels, lacquers, coatings and in grinding vehicles. Its high boiling point, low rate of evaporation and greater solvent strength impart the desirable qualities of better flow, brushing, leveling, spraying and general working qualities. It also retards thickening and skinning, and reduces viscosity. Still other uses are in sterilizing sutures, in printing inks, shoe polishes, blacking and leather dressing, in oil-cloth and linoleum manufacture; and when admixed

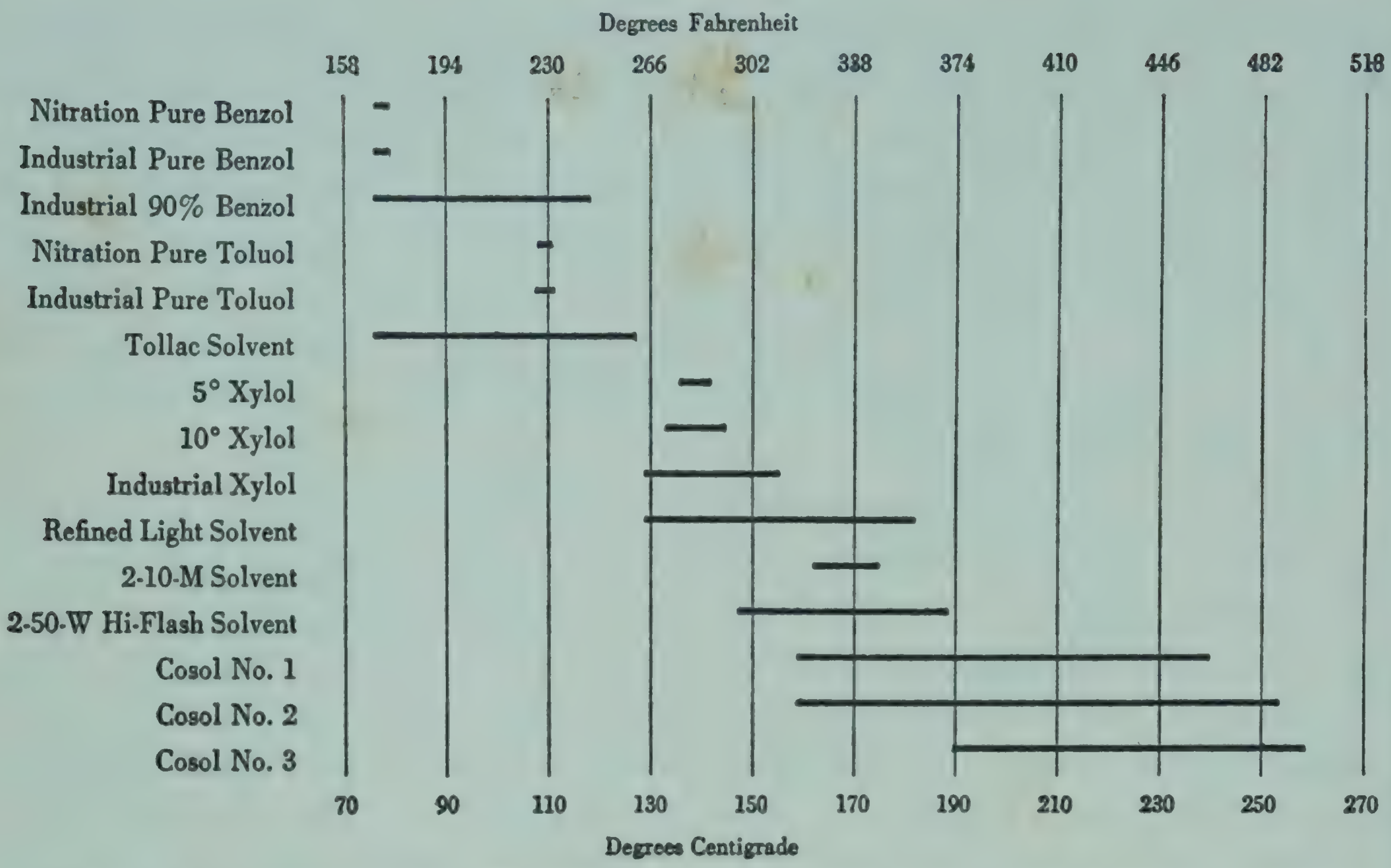


Figure 7.11. Relative Distillation Ranges of Refined Coal-Tar Solvents.[13]

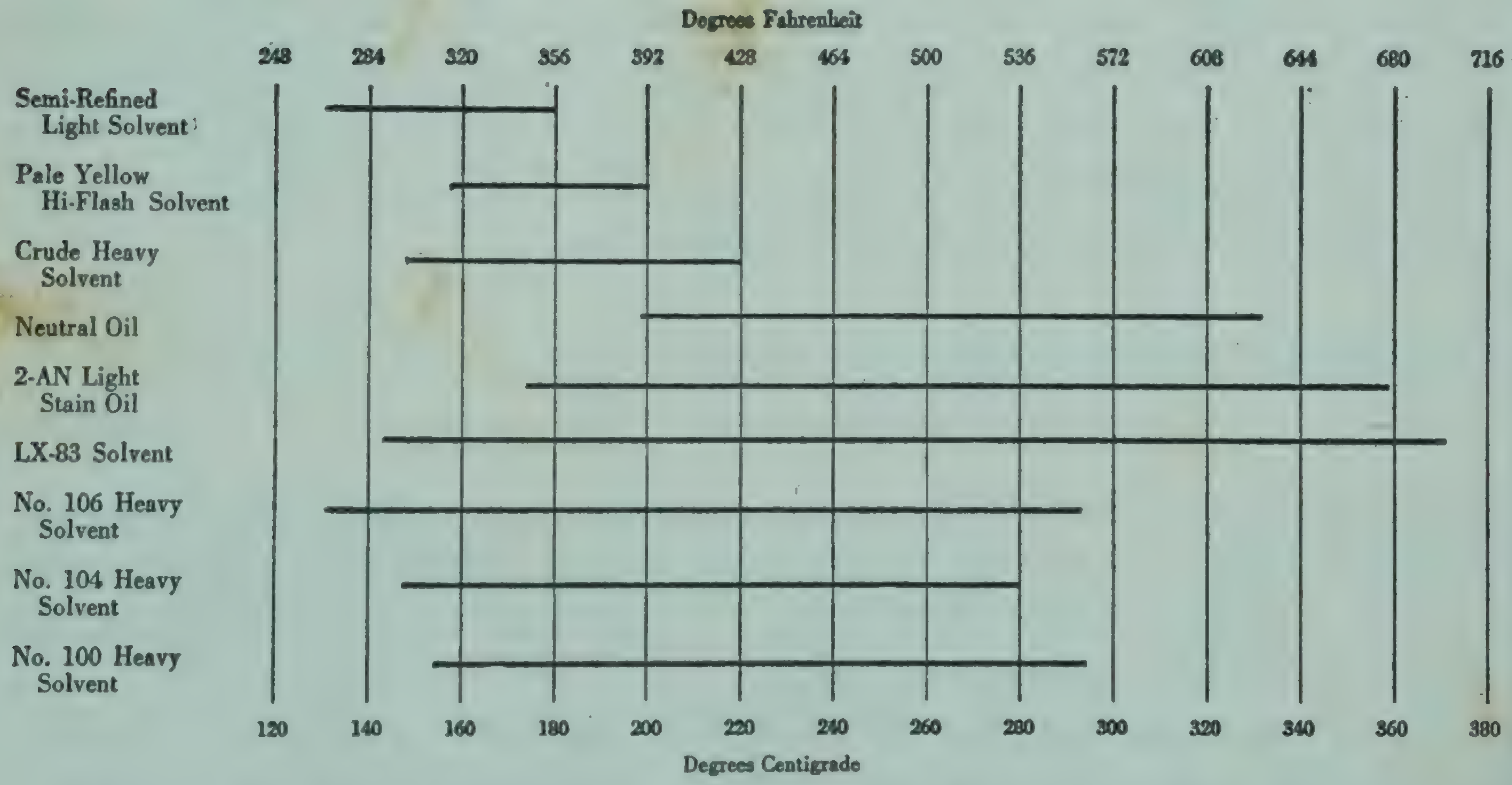


Figure 7.12. Relative Distillation Ranges of Semi-Refined Coal-Tar Solvents.[13]

with alcohol, as a paint and varnish remover. The yellow high-flash naphthas are used in coatings where off color and moderately pronounced odor are not objectionable. Some fractions of naphthas are especially designed as thinners for enamels which are to be applied to copperware, and to secure proper leveling and adhesion of the film at high-temperature baking.

TABLE 7.8. THE BARRETT COMPANY SPECIFICATIONS FOR COKE OVEN LIGHT-OIL DISTILLATES AND COAL-TAR NAPHTHAS

	Distillation							
	First Drop (or Fixed Point)	Per Cent at Fixed Temperature	Dry Point (or Fixed Point) Not above	Color	Specific Gravity at 15.5° C.	Sulfur Compounds as H_2S or SO_2	Solidifying Point	Flash-point approx. (° F.)
Benzenes								
Thiophene free benzene (8)	Not below 79.2° C.	All within 1° C. including 80.2° C.	81.2° C.	Water white	.882 to .886	(1) None	—	10–15
Nitration pure benzene (8)	" " 79.2° C.	" " " " " " "	81.2° C.	" "	.8820 to .8860	None	Not below 4.85° C.	10–15
Industrial pure benzene (8)	" " 78.2° C.	" " 2° " " " "	82.2° C.	" "	.875 to .886	"	—	10–15
Industrial 90% benzene (8)	" " 78.2° C.	At least 90% shall distill at 100° C.	120° C.	" "	.875 to .886	"	—	10–15
Toluenes								
Nitration pure toluene (8)	" " 109.4° C	All within 1° C. including 110.4° C.	111.4° C.	" "	.8690 to .8730	"	—	35–40
Industrial pure toluene (8)	" " 108.4° C.	" " 2° C. " " "	112.4° C.	" "	.864 to .874	"	—	35–40
Xylenes								
Nitration Xylene (8)	" " 137.2° C.	" " 3° C.	140.5° C.	" "	.865 to .870	"	—	80–85
Five degree xylene (8)	" " 137° C.	" " 5° C. including 139.5° C.	143° C.	" "	.860 to .870	"	—	80–85
Ten degree xylene (8)	" " 135° C.	" " 10° C.	145° C.	" "	.860 to .870	"	—	80–85
Industrial xylene (8)	Not above 135° C.	Not over 5% shall distill at 130° C. 90 to 95% shall distill at 145° C.	155° C.	" "	.850 to .870	"	—	80–85
Solvent naphtha	" " " "	" " " " " " "	" "	" "	.850 to .870	"	—	80–85
Industrial Coal-Tar Naphthas								
Cumene	—	95% shall distill between 165.5–175.5° C. 50% point shall be between 169-171° C.	—	" "	—	Not specified	—	Not below 100
Hi-Flash naphtha 185 D.P.	Not below 150° C.	—	185° C.	" " (7)	.855 to .890	None	—	" " "
Hi-Flash naphtha 200 D.P.	" " " "	90% shall distill at approx. 180° C.	200° C.	" " (7)	.855 to .890	"	—	" " "
Crude light solvent naphtha	Not above 135° C.	Not over 5% shall distill at 130° C. 90–95% shall distill at 160° C.	180° C.	Light amber	.860 to .885	Not specified	—	80–90
Crude heavy solvent naphtha	Not over 5% at 150° C.	Not over 5% shall distill at 150° C. Shall distill at least 5% at 165 and 90% to 200° C.	220° C.	Light amber to dark red	.885 to .970	"	Not over 8% dry salts ($C_{10}H_8$)	Not below 100
Heavy naphtha	Shall distill 10% at not below 160° C.	70% point shall be between 195-203° C.	270° C.	Amber to dark red	.915 to .945	"	(4) Not above 10° C.	" " "
Heavy naphtha E. W.	Shall distill 10% at not below 160° C.	" " " " " " "	(5) 270° C.	Straw to dark amber	.915 to .950	"	(6) Below −20° C.	" " "
Special heavy naphtha	Shall distill 10% at not below 160° C.	—	200° C.	Straw to amber	.880 to .970	"	—	" " "

(1) No trace of thiophene or carbon disulfide (3) Tar acids not over 3% by volume (5) Residue shall be a liquid (7) Substantially water-white
(2) Using 60° Bé acid and standing 5 minutes (4) Limpid point, (6) No crystals at —20° C (8) Passes Barrett Copper Corrosion Test

All tests shall be performed in accordance with Barrett Testing Methods as given in Specifications for Coke Oven Light-Oil Distillates.

Other types are used in cleaning compositions, naphtha soaps, in the process of engraving and lithography and in rubber cement.

High-flash naphtha has a higher distillation range than xylene or ordinary solvent naphtha. Analyses indicate its approximate composition:

	% by wt.
Ethyl benzene, xylenes, cumene, propyl benzene, and ethyl toluene	10
Trimethylbenzenes	45
Tetramethyl benzenes	40
Naphthalene	5

The refined product is a liquid of mild odor and high solvent power. It is added to many petroleum thinners to fortify their solvency for natural and synthetic resins, and is used in ordinary enamels, house paints, flat wall and interior paints. It has about the same flash point as turpentine but has a lower rate of evaporation. Pine oil, turpentine and essential oils are often added to this product to give it a fine odor. It is widely used in the field of alkyd resins.

Benzene (C_6H_6) (Benzol, phenylhydride, coal naphtha). Benzene is a hydrocarbon that was first discovered by Faraday in 1825 while he was in the process of compressing illuminating gas. Mitscherlich later prepared it from benzoic acid, and called it "benzin" or "benzine." Liebig proposed the name "benzol", which has been generally adopted for the commercial product. Its presence in coal tar was first discovered by Hofmann in 1834. Benzene is now obtained commercially from coal tar, light oil, illuminating gas and coke-oven gas. The impure grades contain toluene, xylene and a tarry substance.

There are four available grades of benzene: the 90%, which is used for most commercial purposes, the B-refined solvent, the nitration pure, and the industrial pure. The latter have special application where their greater purity, closer boiling range and quicker evaporations are needed.

Benzene is a colorless, mobile liquid having a pleasant and characteristic odor. This solvent is strongly narcotic and toxic and the utmost caution is required in its use. When benzene is used in spraying compounds, especially designed booths and exhaust equipment are required. Its vapor is highly flammable, burning with a very smoky flame, and a benzene-air mixture composed of 1.4 per cent benzene to 4.7 per cent air will explode. It is very slightly soluble in water but is miscible or soluble in ethyl alcohol, ethyl ether, formic acid, glacial acetic acid, carbon tetrachloride, chloroform and carbon disulfide. It is an excellent solvent for a wide range of natural and synthetic resins, gums, waxes, rubber, oleo-resins, aluminum naphthenate, alkaloids, fats, gases and such elements as sulfur, phosphorus and iodine. It dissolves such cellulose ethers as methyl, ethyl, butyl, benzyl celluloses, etc., as well as the following cellulose esters: cellulose dinaphthenate, dilaurate, dipalmitate, distearate, dinitrolaurate, dinitropalmitate and diacetyl-laurate. To increase the solvency of benzene a lower aliphatic alcohol should be added, for example, mixtures of benzene or toluene with ethyl alcohol ranging in ratio from 10:90 to 90:10 can be used to advantage. Adding alcohol to benzene also increases its solvency for gums and resins. Other solvents often used in combination with benzene are acetone, amyl acetate, butyl acetate, benzyl alcohol, carbon tetrachloride, and ethylene glycol.

Benzene is used in the manufacture of synthetic dyes and drugs, photographic film, artificial leather, paper finishes, linoleum and oil-cloth, and in rubber and plastic products. It is also used to enrich gases, and in electrotechnics. Large quantities of benzene are used as a solvent in varnishes, quick-drying asphalt, coal-tar coatings and as a diluent in the lacquer industry; as an antidetonant or knock suppressor in airplane dopes; as a substitute for acetylene in autogenous welding; in the purification of paraffin, waxes and resins; in the process of engraving and lithographing; and as a preservative in sizings of starch and albumin. It is a constituent part of prepared waxes, traffic paints, rubber cement, tire paint, special textile soaps, penetrating stains and motor fuels. When combined with alcohol it is used in spirit stains and with acetone as a paint and varnish remover. Benzene has been used[9] as a solvent in cryoscopic determinations of molecular weight.

Typical Specifications for Commercial Grades

	90%	*Nitration*	*Industrial*	*Refined*
Distillation range	Entirely between 78.2° C and 120° C at least 90% at 100° C	Entirely within 1°C including 80.2° C	Entirely within 2° C including 80.2° C	Entirely within 77.5° C and 150° C at least 90% at 120° C
Specific gravity at 15.6/15.6°	0.875–0.886	0.882–0.886	0.875–0.886	0.870–0.886
Acid wash	Not darker	Not darker than 2	Not darker than 3	Not darker than 12
Acidity	None	None	None	None
Color	Water - white. Not below +25 Saybolt	Water - white. Not below +25 Saybolt	Water - white. Not below +25 Saybolt	Water - white. Not below +25 Saybolt
Corrosion	Passes copper strip test	Passes copper strip test	Passes copper strip test	Passes copper strip test
Flash point	Below 20° F	Below 20° F	Below 20° F	Below 20° F
Freezing point	−8° to +4° C			−8° to 0.0° C
Sulfur compounds	No H_2S or SO_2	No H_2S or SO_2	No H_2S or SO_2	No H_2S or SO_2
Solidifying point	Solid below 5° C			
Average weight per gallon at 15.6° C.	7.33 lbs.	7.36 lbs.	7.33 lbs.	7.31 lbs.

Toluene ($C_6H_5CH_3$) (Toluol, methylbenzene, phenylmethane). Toluene is a colorless, mobile liquid with a benzene-like odor. It was discovered by Pelletier in 1838 and three years later Sainte-Claire Deville prepared it by the distillation of Balsam of Tolu, whence its name. It is obtained principally by the fractional distillation of coal-tar light oils, although increasing amounts are now being produced from petroleum. The vapors of toluene are less toxic than those of benzene, as well as being less flammable and having a slower rate of evaporation. Toluene also evaporates twice as fast as butyl acetate and four times as fast as *n*-butyl alcohol. It is miscible with ethyl alcohol, benzene, ethyl ether, etc. Toluene is a very efficient solvent for gums and such resins as benzyl abietate, copals, copal esters, coumarone resins, glyptal resins, sandarac, vinyl resins, alkyd resins, etc. It is a solvent for various oils, some types of cellulose acetate, many types of cellulose ethers, chlorinated rubber, as well as many dyes and printing ink resins.

There are three grades of toluene commercially available: nitration grade toluene serves the need for a highly pure product; the 90/120 grade toluene is used where extreme purity is not necessary; and industrial pure toluene is the grade most generally used.

Toluene is one of the most widely used hydrocarbon diluents in the lacquer industry, especially in cellulose ester lacquers. The solvency of toluene for cellulose derivatives can be increased by adding ethyl or methyl alcohol. Its uses and applications in the industries are similar to those for benzene. The wartime end-use pattern for toluene is shown in Table 7.9.

TABLE 7.9. TOLUENE IN WORLD WAR II*
Allocations of Toluene: January 1, 1943–June 30, 1945
(Thousands of gallons, pure)

	TOTAL		Jan. 1–June 30, 1945	July 1–Dec. 31, 1944	Jan. 1–June 30, 1944	July 1–Dec. 31, 1943	Jan. 1–June 30, 1943
	Amount	Per cent					
Total Allocations	521,274	100.0	129,533	120,337	115,862	85,114	70,428
Direct military[1]	399,980	76.7	120,176	85,428	56,815	73,846	63,715
Foreign	9,572	1.8	13	21	46	4,950	4,542
Other uses	111,722	21.5	9,344	34,888	59,001	6,318	2,171
Aviation gasoline including military	90,425	17.4	4,196	30,282	53,784	2,163	0
Protective coatings including saturants and solvents	11,781	2.3	2,551	2,535	3,169	2,459	1,067
Miscellaneous[2]	9,516	1.8	2,597	2,071	2,048	1,696	1,104

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[1] End-use data not available.

[2] Includes medicinal, chemical, and research uses; dyes, preservatives, and small lot sales.

* "Facts for Industry", May 29, 1946.

Typical Specifications for Commercial Grades

	Nitration	*Industrial*	*(90/120)*	*Technical*
Distillation range	Entirely within 1° C including 110.5° C	Entirely within 2° C including 110.5° C	Entirely between 100° C and 150° C	
Sp. gr. at 15.6/15.6° C 60/60° F	0.869–0.873	0.864–0.874	0.865–0.875	0.871
Acid wash	Not darker than 2	Not darker than 4	Not darker than 7	
Acidity	None	None	None	
Color	Water - white. Not below +25 Saybolt	Water - white. Not below +25 Saybolt	Water - white. Not below +25 Saybolt	
Corrosion	Passes copper strip test	Passes copper strip test	Passes copper strip test	
Density of liquid at 60° F				7.26 lb. per gallon
Flash point	Below 45° F	Below 45° F	Below 45° F	
Refractive index at 20° C				1.496
Sulfur compounds	No H_2S or SO_2	No H_2S or SO_2	No H_2S or SO_2	
Average weight per gallon at 15.6° C	7.25 lbs	7.24 lbs	7.25 lbs	

Toluene Substitutes. "Nevsol" is a proprietary hydrocarbon, mostly aromatic in character. It is a water-white, flammable liquid used as a substitute for toluene. In certain processes its more rapid evaporation rate may require the addition of small amounts of butyl or amyl alcohol. It is used as a diluent in the lacquer industry.

"Tollac" is a hydrocarbon, mostly aromatic in nature. Like "Nevsol", it is a water-white, flammable substitute for toluene. Having a more rapid evaporation rate it may require the presence of small amounts of amyl or butyl alcohol when used in certain coatings. It is used as a replacement for toluene in the lacquer industry.

"Tollac"

Distillation range	°C	°F
Initial boiling point	81–85	177.8–185.0
20%	86–89	186.8–192.2
50%	89–93	192.2–199.4
90%	108–115	226.4–239.0
Dry	127–132	260.6–269.6

Specific gravity at 15.6/15.6° C	0.840–0.850
Aniline point	27–30° C
Corrosion	Negative (copper dish method)
Dilution ratio (8.3% N.C.)	2.70–2.75
Weight per gallon	6.995 to 7.078 lbs.
Flash point	Below 20° F

TABLE 7.10. Solubility of Various Dyes in Toluene[10]

DYE	MINIMUM CC. TOLUENE TO DISSOLVE 0.5 GRAM DYE	DYE	MINIMUM CC. TOLUENE TO DISSOLVE 0.5 GRAM DYE
Oil Maroon	5	Scarlet RR	15
Scarlet H	5	Naphthol Black	15
Indiana Red	5	Sudan III	16
Butter Yellow	5	Azo Turkey Red	16
Maroon I	5	Sudan R	16
Scarlet M	5	Sudan Brown	16
Chrome Fast Yellow	5	Xylidine Brown M	20
Sudan II	5	Maroon II	20
Sudan VII	5	Maroon III	20
Xylidine Red N	5	Oil Brown	25
Sudan I	6	Benzidine Puce	25
Walnut	6	Alizarin Scarlet	30
Rose	6	Sudan VII	30
Azo Coccine RR	6	Congo Red A	30
Oil Scarlet	7	Cloth Red BB	35
Spirit Yellow	7	Aniline Yellow G	35
Naphthol Brown	7	Cloth Red G	35
Xylidine Brown	7	*p*-Nitroaniline Red	40
Xylidine Red	10	Cardinal	40
Sudan VII	10	Alizarin Yellow GG	50
Sudan IX	10	Sudan G	50
Sudan X	10	Chrysamine G	75
Naphthol Brown II	15	Benzidine Puce A	95
Fast Brown O	15	*m*-Nitroaniline Orange	100
		Benzidine Brown	150 Inc.

"Nevsol"

Distillation range	°C	°F
Initial boiling point	80.6–83.3	177–182
20%	85.4–86.0	185.7–186.8
50%	86.1–90.6	187–195
90%	115.6–121.1	240–250
Dry	132.2–137.8	270–280

Specific gravity at 15.6/15.6° C	0.820–0.830
Aniline point	30–32° C
Color	Water-white
Corrosion	Negative (copper dish method)
Dilution ratio	2.30–2.40 at 0.3% (N.C.)
Weight per gallon	6.83–6.91 lbs.

Xylene [$C_6H_4(CH_3)_2$] (xylol, dimethylbenzene, solvent naphtha). Xylene is a colorless, mobile liquid which exists in three isomeric forms in the light-oil fraction of coal-tar distillates. The industrial grade is a mixture of the three isomers, with the meta compound predominating. Other impurities present in small quantities are toluene, ethyl benzene and pseudocumene (trimethylbenzene). The lower-boiling impurities accordingly reduce the boiling point of xylene and the higher ones retard evaporation. The evaporation rate for xylene is similar to that of amyl acetate, and when compared with benzene or toluene it has a slower rate than either with a correspondingly lower solvent power. The solvent power of this homologous series is similarly altered as in other homologous series by the difference in molecular weight; that is, an increase in molecular weight within the homologous groups results in a corresponding decrease in its solvent action. Xylene is also similar to the lower members of this group by showing an increased solvent power for cellulose esters and ethers when a lower aliphatic alcohol is added. It is soluble in ethyl alcohol, ethyl ether, hydrocarbons, etc. It is used in place of benzene or toluene wherever a slower rate of evaporation is desired.

There are three commercial grades of xylene, the 5 degree, the 10 degree and industrial xylene, each serving needs according to their differences of *properties*. Xylene is used as a diluent in nitrocellulose lacquers, as a solvent for alkyd resins and other natural and synthetic resins and gums, as a

TABLE 7.11. XYLENE IN WORLD WAR II
Allocations of Xylene: July 1, 1944–June 30, 1945*
(Thousands of gallons)

USE	AMOUNT	PER CENT
Total Allocations	95,770	100.0
Direct military[1]	916	0.9
Foreign	59	0.1
Other uses	94,795	99.0
Aviation gasoline blends[2]	70,270	73.4
Protective coatings	18,717	19.6
Medicinals	1,184	1.2
Inks, dyes, intermediates	684	0.7
Adhesives and cements	670	0.7
Cleaning fluids	493	0.5
Miscellaneous uses and small orders	2,777	2.9

[1] End-use data not available.

[2] Includes military aviation fuel.

* "Facts for Industry".

solvent for dyes, printing inks, synthetic perfumes, in vinyl resin finishes and as a thinner in insulating varnishes and wire enamels. It improves the leafing effect of aluminum paints, is useful in raw wool scouring operations, in the manufacture of soaps, and is an efficient solvent for chlorinated rubber. Its good wetting properties make it useful as a dispersant of such pigments as carbon black.

	5°	10°	Ind.
Distillation range	Entirely between 137° and 143 C. 100% within 5° C	Entirely between 135° and 145° C. 100% within 10° C	5% max. at 130° C and 90–95% at 145° C. End point not above 155° C
Spec. gr. at 15.6/15.6° C.	0.860–0.870	0.860–0.870	0.861
Acid wash	Not darker than 6	Not darker than 6	Not darker than 10
Acidity	None	None	None
Color	Water-white. Not below +25 Saybolt	Water-white. Not below +25 Saybolt	Water-white. Not below +25 Saybolt
Corrosion	Passes copper strip test	Passes copper strip test	Passes copper strip test
Flash point	80° to 85° F	80° to 85° F	75° to 85° F
Sulfur compounds	No H_2S or SO_2	No H_2S or SO_2	No H_2S or SO_2
Average weight per gallon at 15.6° C	7.20 lbs.	7.20 lbs.	7.20 lbs.

Solvent Naphthas. *Light Grades.* The light grades of solvent naphtha have boiling points ranging from 110 to 160° C. They are miscible with acetone, amyl alcohol, ethyl alcohol and hydrocarbons. They are solvents for natural and synthetic gums and resins such as ester gum, copal ester, benzyl abietate and benzyl resins, oils, bitumen, rubber and many cellulose ethers. Solvent naphtha has found wide application in the paint and varnish industry in coatings based on coal-tar pitch, stearin pitch, petroleum pitch, asphalt, and cold-cut East India gum. The close-cut, high-boiling naphtha fractions are used as diluents in cellulose ester lacquers, in flat varnishes, antifouling paints, synthetic coatings, and in plastics and moldable masses. They are solvents for aluminum stearate in waterproofing and are used as thinners in gold and aluminum bronzes, in penetrating stains and in paint, varnish and finish removers. By adding them to phenol resins, Congo varnishes and similar mixtures, skinning and gelling are prevented. They also increase solvency when used in conjunction with petroleum solvents.

Heavy Naphthas

(Range of Specifications of Various Grades)

Distillation range	150° C–290° C
Flash point	80°–110° F
Distillation residue	Oil, no pitch
Specific gravity at 15.6/15.6° C	0.875–0.945
Color	Light amber (Amber)
Tar acids	Free from any objectionable quantities
Weight per Gallon at 15.6° C	7.78 lbs.

High-Flash Naphtha

Distillation range	Entirely between 148° C and 190° C. 30–40% at 160° C
Flash point	Not below 95° F
Acidity	None
Corrosion	Passes Copper strip test
Color	Water-white. Not below +21 Saybolt.
Naphthalene	None
Specific gravity at 15.6/15.6° C	0.860 to 0.875
Weight per gallon at 15.6° C	7.22 lbs. (average)

Refined Naphtha

Distillation range	Entirely between 163°–177° C
Flash point	Not below 115° C
Specific gravity at 15.6/15.6° C	0.865 to 0.880
Acidity	None
Color	Water-white
Weight per gallon at 15.6° C	7.19 lbs. (average)

Semi-refined Naphtha

Distillation range	160°–200° C
Flash point	Not below 110° F
Specific gravity at 15.6/15.6° C	0.865 to 0.885
Acidity	None
Color	Very light straw (not below +10 Saybolt)
Sulfur compounds	No H_2S or SO_2
Weight per gallon at 15.6° C	7.29 lbs. per gal. average

High-Boiling Crude Naphtha (Shinge Stain Oil)

Distillation range	140°–350° C (Not more than 20% at 200° C)
Corrosion	Passes copper strip test
Color	Dark red
Specific gravity at 15.6/15.6° C	0.970 to 0.995
Weight per gallon at 15.6° C	7.83 lbs. (average)

Alkylated Aromatic Hydrocarbons

Ethylbenzene (phenylethane) ($C_6H_5 \cdot C_2H_5$). Ethylbenzene is a colorless, mobile liquid with a pleasant odor. It is soluble in ethyl alcohol, ethyl ether, benzene, carbon tetrachloride, and hydrocarbons, but insoluble in water. Ethylbenzene is similar to xylene in solvent power and in some of its physical and chemical properties. It is used as a solvent for synthetic resins, as a diluent in lacquers and in organic synthesis. Mixtures of this solvent with lower aliphatic alcohols or lower alkyl acetates have been proposed as blending agents for cellulose ethers.

Boiling point	136.4° C
Boiling range	3.0° C
Specific gravity at 25/25° C	0.866
Fire point	21° C
Flash point	20° C
Freezing point	−70° C
Melting point	−94° C
Dielectric constant, 1000 cycles	2.3
Power factor, 1000 cycle	0.84%
Refractive index at 25° C	1.493
Specific heat	0.41 cal./gm./° C
Specific restivity	3.6×10^{12} ohms/cm.
Solubility in water at 15° C	0.014
Viscosity at 25° C	0.63 centipoise
at 60° C	0.44 "
Weight per gallon at 25° C	7.21

Diethylbenzene $C_6H_4(C_2H_5)_2$. Diethylbenzene is a colorless liquid with a pleasant and characteristic odor. It is insoluble in water but soluble in ethyl alcohol, ethyl ether, benzene and carbon tetrachloride. It is used as a high-boiling solvent and in the manufacture of resins.

Boiling point	181.2° C
Boiling range	3.0° C
Specific gravity at 25/25° C	0.868
Dielectric strength, volts at 0.1″ gap	22,000
Fire point	64° C
Flash point	59° C
Freezing point	70° C
Dielectric constant, 1000 cycle	2.2
Power factor, 1000 cycle	0.05%
Purity	(Approx) 75–80% *o*-diethyl benzene (Approx) 20–25% *m*-diethyl benzene
Refractive index at 25° C	1.493
Specific heat	0.38 Cal./gm./° C
Specific resistivity	4.8×10^{12} ohms/cm.
Viscosity at 25° C	0.86 centipoise
at 60° C	0.57 "
Weight per gallon at 25° C	7.22

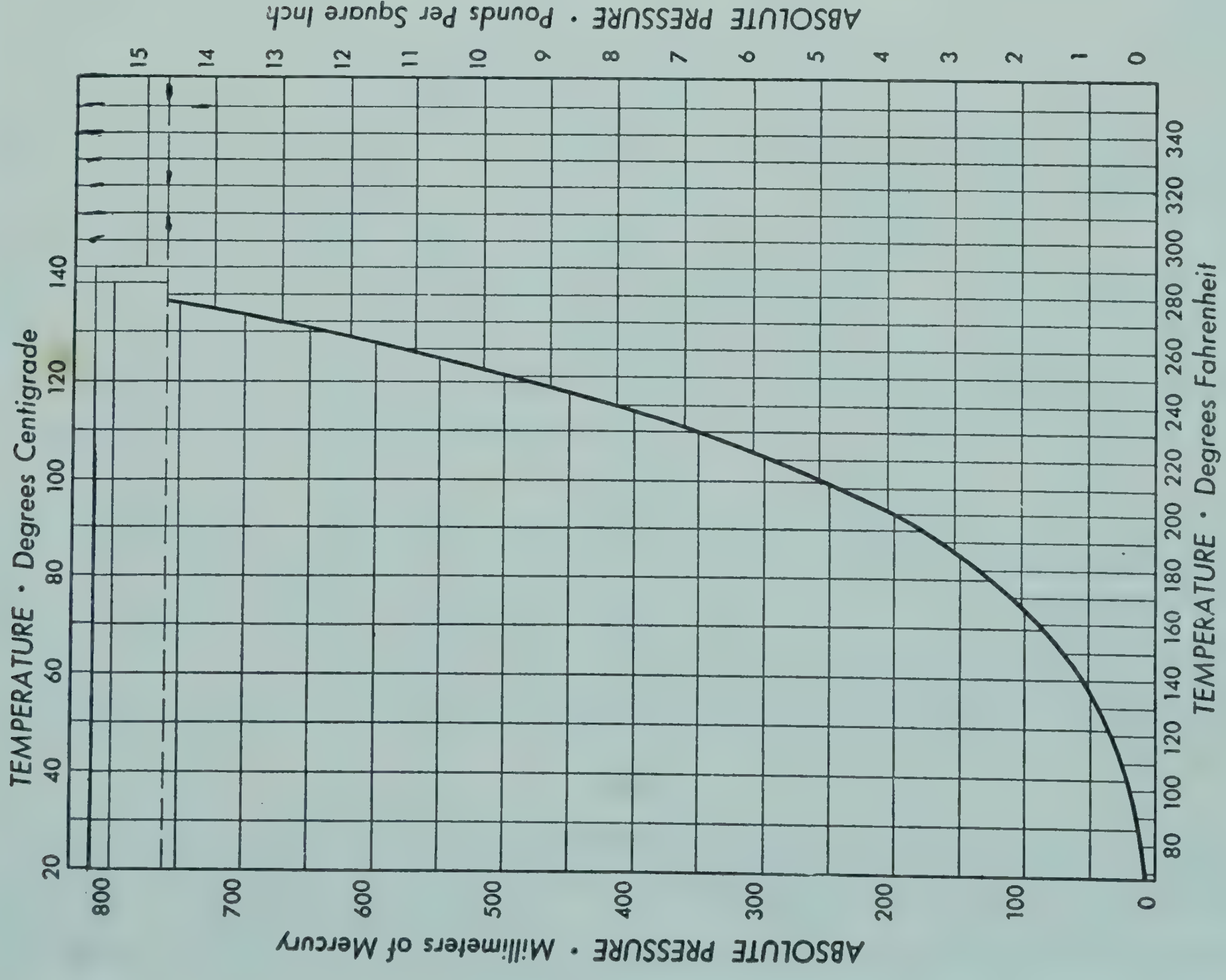


Figure 7.13. Vapor Pressures of Ethyl Benzene[12]

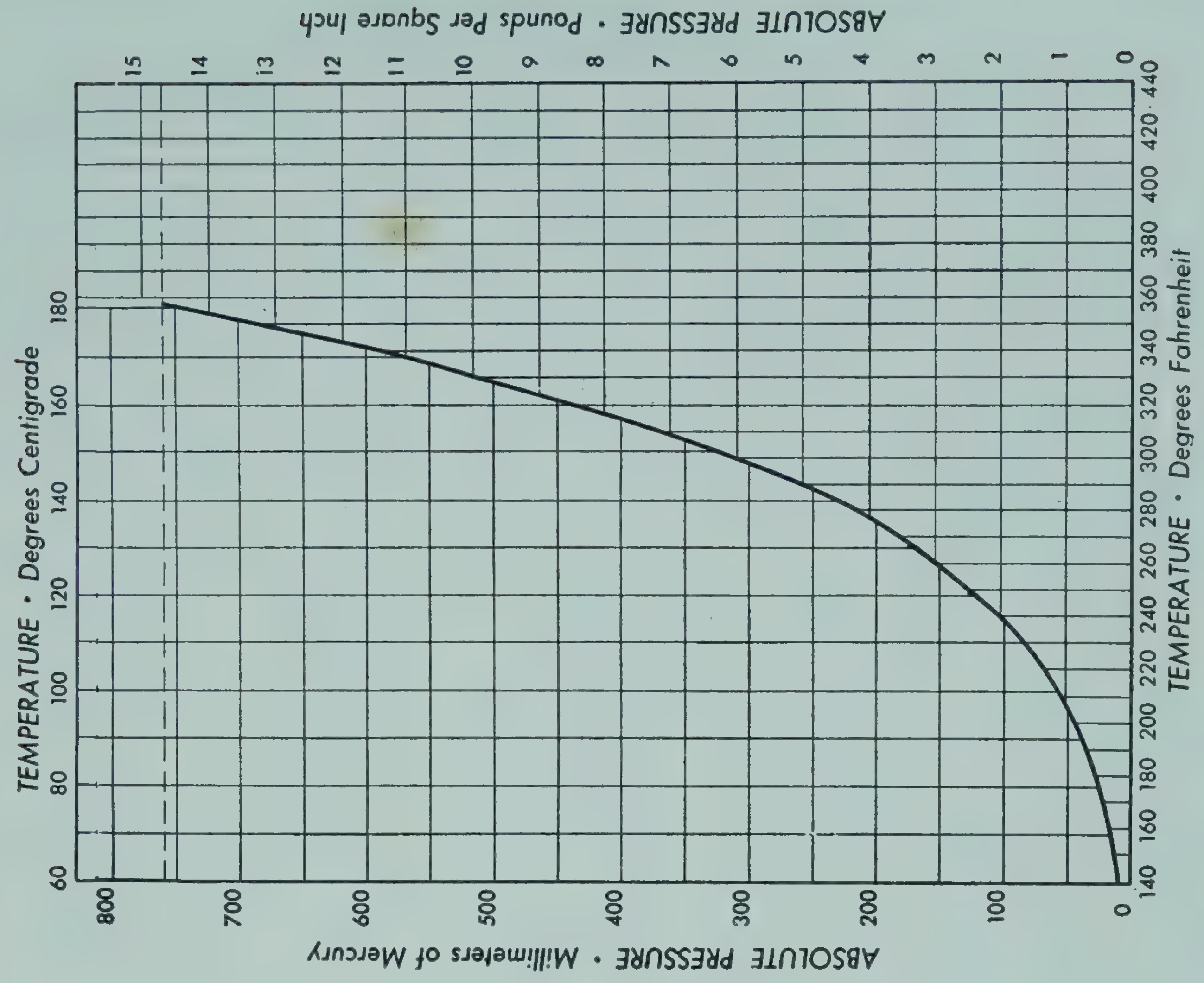


Figure 7.14. Vapor Pressures of Diethyl Benzene[12]

TABLE 7.12. COMPARISON OF PHYSICAL PROPERTIES OF HYDROCARBONS REPORTED BY DIFFERENT OBSERVERS[11]

	o-XYLENE	*m*-XYLENE	*p*-XYLENE	ETHYLBENZENE
Freezing point, ° C	−25.30	−48.56	+13.00	−95.30
Plateau time, min.	21.5	8	7.5	11
Bath composition	CO_2 + isopropyl alcohol	Commercial nitrogen	CO_2 + isopropyl alcohol	Commercial nitrogen
Gradient at F. P., ° C	55	144	93	97
Cottrell spread, initial B. P. to 50% distd., ° C	144.4 to 144.4	139.1 to 139.1	138.5 to 138.6	136.3 to 136.5
d_4^{25a}	0.8759	0.8600	0.8576	0.8624
d_4^{20b}	0.8809	0.8650	0.8626	0.8674
Gravity^b, ° A.P.I.	28.3	31.2	31.6	30.7
Lb./gal. at 60° F	7.39	7.26	7.24	7.28
n_D^{20}	1.5053	1.4970	1.4959	1.4958
Dispersion at 20° C	158.2	155.8	156.5	151.3
Sp. dispersion at 20° C	179.6	180.1	181.4	174.4
Du Noüy surface tension at 25° C, dynes/cm.	31.56	30.46	29.95	30.50
Dielectric constant at 30.05° C	2.571	2.351	2.264	2.382
Bureau of Standards Values (*14*)				
Freezing point, ° C	−25.30	−47.55	+13.35	...
Boiling point, ° C	144.4	139.3	138.4	...
d_4^{20}	0.88040	0.86401	0.86100	...
Boord and Henne Values (*4*)				
Freezing point, ° C	−25.5	−48.9	+13.19	−94.96
Boiling point, ° C	144.5	139.2	138.5	136.5
n_D^{20}	1.5054	1.4971	1.4958	1.4959
d_4^{20}	0.8799	0.8639	0.8609	0.8661
Estd. impurities, mole fraction	0.010 ± 0.003	0.026 ± 0.009	0.0010 ± 0.0005	0.006 ± 0.002

[a] 10-cc. pycnometer at 25° ± 0.002° C.

[b] Coefficient of cubical expansion of all four C_8 aromatics taken as 0.0010.

Triethylbenzene $C_6H_3(C_2H_5)_3$. Triethylbenzene is a colorless liquid with a mild odor. It is insoluble in water but soluble in ethyl alcohol, benzene and carbon tetrachloride. It is used as a heat-transfer medium, as a dielectric fluid, as a solvent and as an intermediate.

Boiling point	218° C
Specific gravity at 25/25° C	0.870
Dielectric strength	23,000 v.
Fire point	90° C
Flash point	83° C
Freezing point	−70° C
Dielectric constant, 1000 cycles	2.2
Power factor	0.05%
Refractive index at 25° C	1.498
Specific heat	0.4 cal./gm.
Specific resistivity at 60° C	0.0
Viscosity at 25° C	1.31 centipoise
at 60° C	0.79 "
Weight per gallon at 25° C	7.2 lbs.

TABLE 7.13. SOLVENCY PROPERTIES[11]

	o-XYLENE	*m*-XYLENE	*p*-XYLENE	ETHYLBENZENE
Kauri-butanol value, cc.	106.8	102.8	97.3	98.6
Kauri-butanol solvent power[a]	97.7	94.0	89.2	90.3
Solvent power by wt.[a]	85.5	80.8	76.4	77.8
Kauri-butanol solvency[b]	101.9	98.4	93.2	94.5
Mixed aniline point, ° C.[c]	8.4	10.0	10.6	10.0
Polybutene *n*-decanol value, ml.[d]	12.38	12.40	11.72	11.70
Maleic resin solvency, ml.[e]	44.0	37.5	36.7	42.2

[a] Benzene = 100; *n*-heptane = 25.4 (*1*, *2*).

[b] Toluene = 100; primary reference mineral spirits = 40 (*9*).

[c] Critical solution temperature of 10 ml. anhydrous aniline, 5 ml. of C_8 aromatic, and 5 ml. of a 60° C. aniline point naphtha of 43°/44° A.P.I. gravity—i.e., a naphtha which gives a 10.0° C mixed aniline point with pure toluene (*7*, *11*).

[d] Tolerance, to cloud point at 25° C, of a solution of 2.0 grams of 5500 molecular weight polybutene in 10 ml. of C_8 aromatic (*8*).

[e] Ml. of 60° C aniline point naphtha tolerated at 25° C by a solution of 10.0 grams Amberol 801 in 40 grams C_8 aromatic (*7*).

Isopropylbenzene (Cumene, Cumol) ($C_6H_5C_3H_7$). Isopropylbenzene is a colorless liquid, soluble in ethyl alcohol, ethyl ether, benzene and carbon tetrachloride, and has a narrower distillation range than ordinary high-flash naphtha. It is used as a lacquer diluent, in sterilizing catgut and in organic synthesis.

Boiling point	152.3° C
Boiling range	3.0° C
Specific gravity at 25/25° C	0.861
Dielectric strength, volts at 0.1″ gap	21,000
Fire point	38° C

Flash point	36° C
Freezing point	−70° C
Dielectric constant, 1000 cycles	2.3
Power factor, 1000 cycles	0.05%
Refractive index at 25° C	1.489
Specific resistivity	0.43 cal./gm./° C = (calculated) 8.6 × 10^{12} ohms/cm.
Weight per gallon at 25° C	7.19

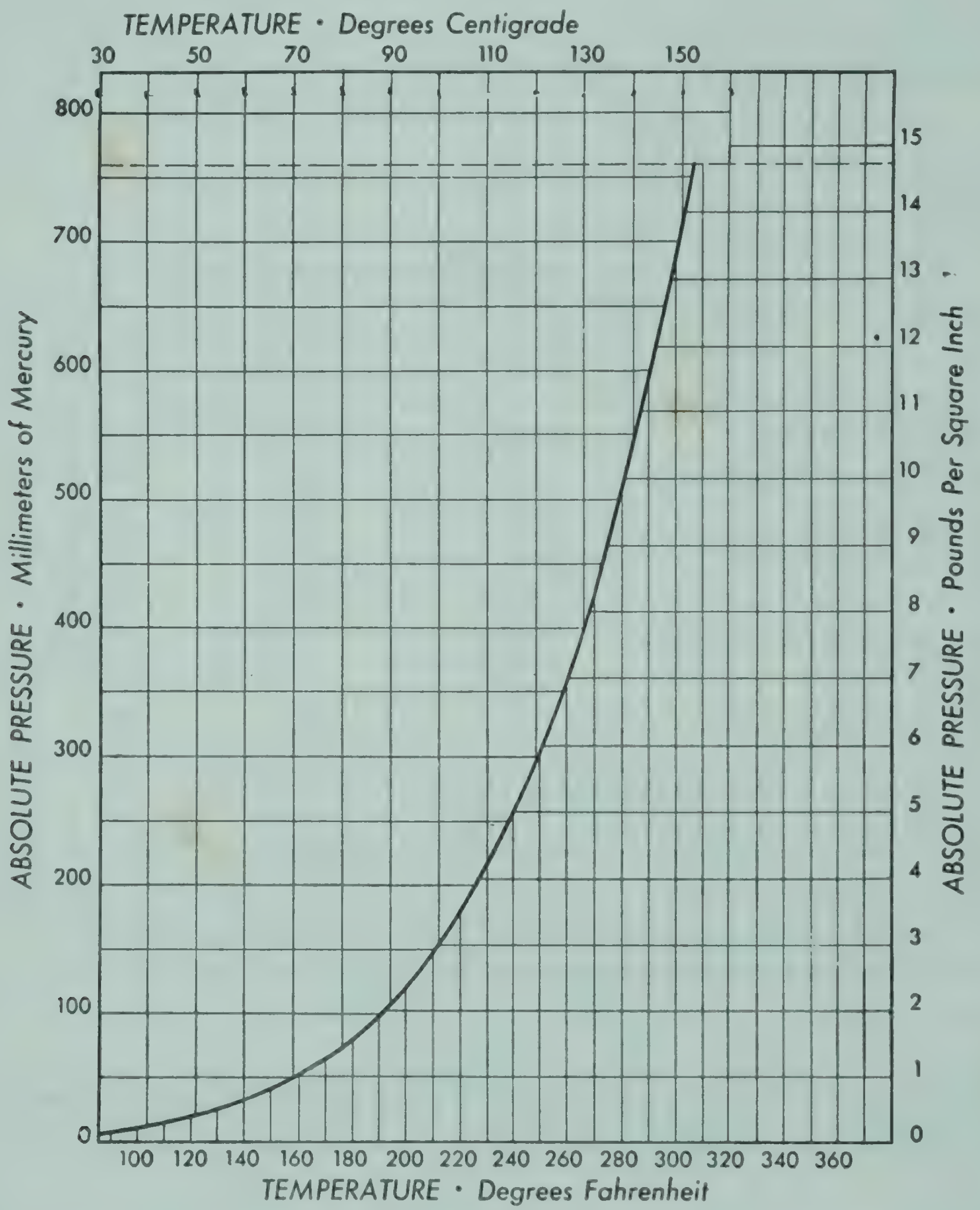


Figure 7.15. Vapor Pressures of Isopropyl Benzene[12]

Amylbenzene ($C_6H_5C_5H_{11}$). Amylbenzene is a water-white liquid with an aromatic odor. The commercial product contains about 10 per cent of secondary and tertiary amylbenzenes. It is soluble in ethyl alcohol, ethyl ether, ethyl acetate, acetone, fixed oils, mineral oil, oleic acid, aromatic and aliphatic hydrocarbons and stearic acid when hot. It is also solvent for paraffin wax and carnauba wax, when hot. Amylbenzene is insoluble in water and methyl alcohol. It finds application as a medium boiling vehicle and plasticizer in inks, vitrifiable colors and synthetic resins.

Boiling range	185–195° C
Specific gravity at 20/20° C	0.874
Distillation range	185–195° C
Flash point	150° F
Refractive index at 20° C	1.4880
Solidification point	Below −75° C
Weight per gallon	7.28 lbs.

Diamylbenzene $C_6H_4(C_5H_{11})_2$. Diamylbenzene is a water-white liquid with an aromatic odor. The commercial grade contains about 90% *sec.*-amylbenzene and the remainder *tert.*-amylbenzene. It is soluble in ethyl ether, ethyl acetate, acetone, fixed oils, mineral oil, oleic acid and aromatic and aliphatic hydrocarbons. It is insoluble in water and methyl alcohol. When hot it is a solvent for paraffin wax, carnauba wax and stearic acid.

Boiling range	260–280° C
Specific gravity at 20/20° C	0.86
Distillation range	260–280° C
Flash point	225° F
Refractive index at 20° C	1.4837
Solidification point	Below −75° C
Weight per gallon	7.16 lbs.

Triamylbenzene $C_6H_3(C_5H_{11})_3$. Triamylbenzene is a water-white liquid with a faintly aromatic odor. It is soluble in ethyl ether, ethyl acetate, acetone, fixed oils, mineral oil, oleic acid and aromatic and aliphatic hydrocarbons. Paraffin wax, carnauba wax and stearic acid will dissolve when hot. This solvent is insoluble in water and methyl alcohol.

Boiling range	300–320° C
Flash point	270° F
Specific gravity at 20/20° C	0.87

Tetraamylbenzene $C_6H_2(C_5H_{11})_4$. Tetraamylbenzene is a light straw-colored liquid with a faintly aromatic odor. It is soluble in ethyl ether, ethyl acetate, acetone, fixed oils, mineral oil, oleic acid and aromatic and aliphatic hydrocarbons. When hot, it will dissolve paraffin wax, carnauba wax and stearic acid. It is insoluble in water and methyl alcohol.

Boiling range	320–350° C
Flash point	295° F
Specific gravity at 20/20° C	0.89

Dikerylbenzene-12 (Didodecyl Benzene). Didodecyl benzene is a light straw-colored, almost odorless liquid soluble in ethyl ether, ethyl acetate, acetone, fixed oils, mineral oil, oleic acid and aromatic and aliphatic hydrocarbons. It is a solvent for paraffin wax, carnauba wax and stearic acid at higher temperatures. It is insoluble in water and methyl alcohol.

Boiling range	359–429° C
Flash point	320° F
Specific gravity at 20/20° C	0.942

Amyltoluene ($C_5H_{11}C_6H_4CH_3$). Amyltoluene is a light straw-colored liquid with an aromatic odor. It is soluble in ethyl ether, ethyl acetate, acetone, fixed oils, mineral oil, oleic acid, hot stearic acid and aromatic and aliphatic hydrocarbons. It is also a solvent for paraffin wax and carnauba wax when hot. It is insoluble in water and methyl alcohol.

Boiling range	206–214° C
Flash point	180° F
Specific gravity at 20/20° C	0.87

HYDROGENATED HYDROCARBONS

Cyclohexane (hexahydrobenzene, hexamethylene, hexanaphthene, benzene hexahydride). $(CH_2—CH_2—CH_2—CH_2—CH_2—CH_2)$. Cyclohexane is a water-white, mobile liquid. It has a pungent odor somewhat similar to benzene but it is less toxic. It is made by the catalytic hydrogenation of benzene and is also a constituent of crude petroleum. It is completely miscible with ethyl alcohol and the higher alcohols, ethers, hydrocarbons, chlorinated hydrocarbons, and most lacquer solvents.

It is an excellent solvent for oils, fats, waxes, bitumens, crude rubber, ethylcellulose and resins. It will hold in solution 9 per cent of carnauba wax, 20 per cent of paraffin, or 15 per cent of crepe rubber. It is used in oil and fat extraction, degreasing, for recrystallization purposes, in the molding industry, in the fabrication of glass substitutes composed of wire mesh coated with synthetic resins, in the textile industry, dry cleaning, shoe cleaning products, in the lacquer industry and in paint removers. Having a lower toxicity, it has been used as a substitute for benzene.

Physical Properties and Specifications

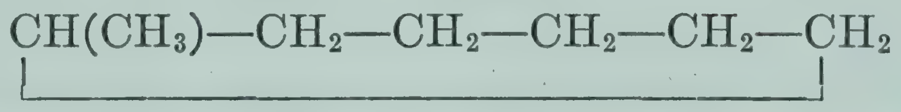
Acidity	Neutral
Boiling point	80.8° C
Color	Water-white
Specific gravity at 20° C	0.780
Distillation range	79.0–82.0°C
Effect on metals	Non-corrosive
Evaporation rate (Toluene = 100)	195
Flammable limits in air	1.3 to 8.4% by volume
Flash point (Open cup)	40°F

Freezing point	6.5°C
Purity	98–100%
Residue from evaporation	None
Refractive index at 25°C	1.423–1.427
Solidification point	37.4°F
Solubility in water at 20°C	Insoluble
Viscosity at 25°C	0.8 centipoise
Vapor pressure at 0°C	27 mm. Hg
20°	77
40°	185
60°	390
80°	740

Azeotropic Mixtures

% by weight cyclohexane		% by weight	B.P. °C
45	Benzene	55	77.8
90	Butanol	10	79.8
70	Ethanol	30	64.9
86	Isobutanol	14	78.1
77	Isopropanol	23	68.6
63	Methanol	37	54.2
80	Propanol	20	74.3
91.6	Water	8.4	69.5

Methylcyclohexane (hexahydrotoluene)

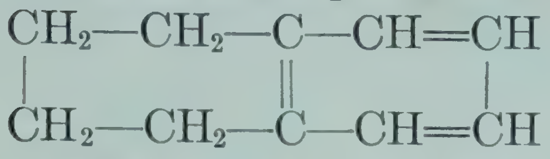


$$CH(CH_3)—CH_2—CH_2—CH_2—CH_2—CH_2$$

Methylcyclohexane, a saturated cyclic hydrocarbon, is a water-white liquid with a characteristic odor. It is soluble in acetone, benzene, ether and carbon tetrachloride. Since its physical properties and many of its uses are quite similar to those of cyclohexane, a choice between them is dependent upon the need in terms of boiling point and evaporation rate.

Acidity	Neutral
Boiling point	101.2°C
Boiling range, 5–95%	100–103°C
Specific gravity at 25°/25°C	0.768
Color	Water-white (less than 20 Hazen)
Distillation range	100.0°–103.0°C
Evaporation rate (Toluene = 100)	140
Fire point	−5°C
Flash point (approx.)	Below 10°F (−5°C)
Freezing point	−120°C
Residue from evaporation	None
Refractive index at 25°C	1.419 = 1.422
Solubility in water at 20°C	Insoluble
Water content	Less than 0.2%
Weight per gallon	6.4 lbs.

Tetrahydronaphthalene (“Tetralin”, 1,2,3,4-tetrahydronaphthalene).



$$\begin{array}{l} CH_2{-}CH_2{-}C{-}CH{=}CH \\ | \qquad\qquad\quad \| \qquad\quad | \\ CH_2{-}CH_2{-}C{-}CH{=}CH \end{array}$$

“Tetralin” is a colorless, pungent liquid made by the catalytic hydrogenation of naphthalene. One ring of this compound is completely hydrogenated while the other is unchanged. With prolonged exposure oxidation will occur, giving a yellow color to the liquid. It is miscible with most organic solvents, especially petroleum thinners. It is a powerful solvent for waxes, oleoresins, gums, oils, resins (coumarone resin, rosin, mastic, alkyd resins, etc.), rubber, resinates, naphthalene, cellulose ethers, linoxyn, asphalt, and the like. Some of its chief uses are as a solvent and thinner in the paint and varnish industry, as a solvent for asphalt, in making bituminous emulsions, in liquid driers, in surface coatings, and as a solvent for metallic soaps. It has a tendency, however, to react with manganese soaps, forming dark-colored compounds. Its high solvent power for oils, short-oil glyptal resins, greases and waxes as well as its detergent properties make it particularly suitable for use in the textile industry, where it is used in combination with textile soaps and oils in such processes as open scouring and kier boiling of cotton, piece goods, wetting and cleaning prior to dyeing, removal of oil from rayon and yarn, and the scouring of fabricated silk and wool.

Having the power to absorb large quantities of naphthalene and gums, “Tetralin” is an excellent solvent medium when used in scrubbers for removal of impurities in gas. Added to gas-distributing systems it gradually dissolves and removes deposits of naphthalene in the pipes and thus prevents corrosive action. It also is a valuable fogging agent. “Tetralin” has been recommended both for removing casinghead gasoline from natural gas and for removing benzene, toluene and naphthalene from coal gas.

“Tetralin” finds considerable use in the printing ink field. Not only is it effective in de-inking paper—a process by which old telephone books are reclaimed—but it is also an ingredient of many special-purpose inks designed for printing on such materials as rubber, leather, and plastics, as well as in quick-drying inks. It is also used in shoe creams, in floor waxes, in motor fuels, in paint and varnish removers, as a solvent for tung oil, as a solvent for chlorinated rubber, in the manufacture of alkali-resistant lacquers and as a turpentine substitute. Its disinfectant and spreading properties are utilized in insecticidal sprays.

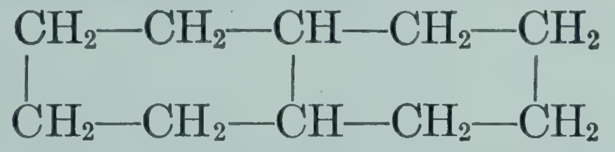
Physical Properties

Molecular weight	132.10
Boiling point	206°C (403°F)
Evaporation rate	Considerably slower than turpentine or high flash naphtha.

Freezing point	−25°C
Heat of combustion (gross)	10,150 cal./g. 18,260 B.T.U/lb.
Refractive index	1.540–1.547
Specific heat	0.463
Surface tension at 180°C.	3.49 mg./mm.
Solubility in water	Insoluble
Viscosity (S.U.V. at 100°F.)	32
Vapor pressure at 20°C.	0.18 mm.

Specifications

Boiling range	207–215°C
Specific gravity at 20°C	0.970–0.975
Color	Water-white
Acidity	Neutral
Flash point (closed cup)	80°C
Moisture content	None
Residue on evaporation	None
Weight per gallon at 20°C	8.10 lbs.

Decahydronaphthalene ("Decalin", "Ketalin", "Decanap", 0,4,4-Decane) 
$$\begin{array}{ccccccccc} CH_2 & — & CH_2 & — & CH & — & CH_2 & — & CH_2 \\ | & & & & | & & & & | \\ CH_2 & — & CH_2 & — & CH & — & CH_2 & — & CH_2 \end{array}$$
"Decalin" is a colorless water-insoluble liquid produced by the complete catalytic hydrogenation of naphthalene. Although similar to tetrahydronaphthalene, it is more stable to atmospheric oxidation. It is miscible with most organic solvents including absolute alcohol, but is not miscible with 95% alcohol. It will not dissolve cellulose nitrate or acetate, cellulose esters, copal and kauri. It is not as powerful as tetrahydronaphthalene, but is a good solvent for oils, fats, waxes, latex, resins such as dammar, mastic and manila and oleoresins, alkyd resins, etc. The uses of "Decalin" are similar to those of "Tetralin" and when these two hydrogenated solvents are mixed, the blend has a more powerful solvency than either of its components.

One of its most important uses is in the preparation of shoe creams and floor waxes, imparting to them a better and greater spreading power and softening the consistency of the paste. Other uses for "Decalin" are as a turpentine substitute, as a stain remover, as a constituent of cleaning fluids, lubricating oils, perfumery, paints, lacquers and varnish removers.

Physical Properties

Evaporation rate	Considerably slower than turpentine or high flash naphtha, faster than tetralin.
Freezing point	−65°C
Refractive index at 20°C	1.467–1.479
Viscosity (S.U.V. at 100°F)	34
Dielectric constant at 25°C	2.11

Specifications

Boiling range	188–195°C
Specific gravity at 20°C	0.885–0.890
Color	Water-white
Flash point (closed cup)	57°C
Acidity	Neutral
Moisture content	None
Residue on evaporation	None
Weight per gallon at 20°C	7.39 lbs.

MISCELLANEOUS AROMATIC HYDROCARBONS

Diphenyl (Biphenyl, Xene) $C_6H_5C_6H_5$. Diphenyl is a yellow solid with a pleasant odor. It is soluble in carbon tetrachloride, slightly soluble in ethyl alcohol, but insoluble in water. It is used as a heat-transfer medium when mixed with diphenyl oxide. Diphenyl derivatives are used in making dyestuffs, insecticides and plastics.

Boiling point	255.0°C
Boiling range, within	2.0°C
Color	Yellow to Amber
Fire point	124°C
Flash point	106°C
Freezing point	Not less than 68.5°C
Heat of vaporization, B.T. U./lb. at B.P.	136.5
Melting point	69.4°C
Specific gravity at 75/4°C	0.991
Specific heat at B.P.	0.60
Weight per gallon at 75°C	8.27 lbs.

Coal-tar Creosote. Coal-tar creosote (creosote oil, liquid pitch oil) is an oily distillate, yellowish to dark green-brown in color, obtained from the high-boiling fractions of crude coal tar. Chemically, it is a mixture of cresols, oxycresols, methyl cresols and other phenols. In specific gravity, these range from 1.03 to 1.10 and distill between 200 and 400°C. They are soluble in alcohol, benzene, toluene, ether, chloroform, volatile oils and so forth. Heavy creosote is used as an absorbent in the recovery of light hydrocarbons from coal-gas.

Its disinfecting properties make it applicable as a preservative for piling, railroad ties and lumber used for the same purpose. It replaces the sap, renders the wood non-absorbent, and inhibits germ life. Beechwood creosote is a colorless to yellow oil with a characteristic smoky odor. Its specific gravity is about 1.08 and it boils between 205 and 220°C. It is used as an antiseptic and local anesthetic. The light types of coal-tar creosote oil are used as shingle stain oil, in pipe coatings and in plastic products formulated from coal-tar pitch. Their behavior is that of a penetrant, wood preservative, and water-repellent. By heating with sulfur in the presence of an oxidizing gas, the solvent properties of this oil are increased for coal.

TERPENE SOLVENTS

Turpentine. Crude turpentine, or the oleoresin, is the oldest solvent known, its history dating back to civilizations even beyond the Egyptians. The ancients employed this material as a vehicle for the natural earth colors, with which they drew pictures and colored clothing materials. There was comparatively little change until recently in the method of collecting the oleoresin, which was taken from living trees during the spring and summer and in the late autumn. As a result of comparatively recent application of the solvent extraction process, in the last ten years an estimated 10,000,000 tons of forest waste has been reclaimed. Among the products made commercially available by the latest developments in solvent extraction, are turpentine, terpenes, isomeric terpinenes, terpinolene, pine oil, fatty acids, rosin oils, and such pure substances as alpha-pinene, beta-pinene, *p*-cymene, *p*-menthane, *tert*-tolylcarbinol, alpha-methyl-*p*-methyl styrene, *p*-methylacetophenone, cumic acid, "Beta-terpineol", oleic acid, rosin acids, and isoprene. Hercules turpentine contains about 90 per cent dextro-alpha-pinene, and the remainder is composed of moncyclic terpene hydrocarbons, most of which is dipentene.

Gum turpentine, gum spirits, spirit of turpentine, turpentine and oil of turpentine are names given to natural turpentine. This highly mobile, flammable liquid is obtained by the steam distillation of oleoresins obtained from coniferous trees (pine tree family). Chemically, turpentine is composed of alpha- and beta-pinene, dipentene, terpinenes, borneol, fenchyl alcohol, limonene and traces of camphor. The natural turpentines have common physical properties which vary within reasonable limits; but their chemical constituents vary with the source of the oleoresin, the method of distillation and the degree of oxidation and polymerization which they have undergone. Spirit of turpentine is an excellent solvent for oils of all kinds, oleoresins, metallic soaps, blown oil, fossil gums and so forth, and is used in surface coatings as primers, flat paints, varnishes and enamels. Its presence imparts penetration to a solution of metallic soaps and to priming coats, and clarity to dammar varnishes. As a solvent, turpentine is used in slack-melt varnishes—short-oil varnishes made from kauri, manila and so forth. The wetting qualities of turpentine are a desirable property in coating mixtures. Turpentine thus finds application both in coatings where the pigments are required to be held in suspension and in grinding varnishes. It also imparts brilliancy, flowing qualities and good working properties.

Wood turpentine is made by the steam distillation of dead pine wood. Chemically it is a mixture of 85 per cent alpha-pinene, the remaining portion consisting largely of dipentene. This larger amount of dipentene imparts better wetting qualities and greater solvent power than gum turpentine. The predominance of alpha-pinene gives it a narrower distillation range than that of spirit of turpentine, although the rate of evaporation is about the same. For industrial us, however, these two products are interchangeable.

Wood turpentine, made by the destructive distillation of pine tree stumps, is a rather crude grade of turpentine and contains more impurities. It is dark in color, stronger in odor and more powerful in solvent action. When this is refined it is used in lower grades of paints, varnishes and enamels. It also finds use in stains and asphalt paints. The wetting and penetrating power of turpentines carries the paint or varnish below the applied surface and in so doing binds it sufficiently to prevent peeling off. Turpentine vapors may cause nausea, irritate the skin, and will corrode copper, iron and other metals.

Even more varied, both in sources and in uses than natural turpentines, are the synthetic and substituted substances. While these three types differ chemically, all have one important characteristic—a common solvent power.

Unlike the substituted turpentines, the synthetic types have chemical properties somewhat similar to the natural products. Both synthetic and natural turpentines contain chemicals related to the terpene group. On the other hand, the substitute materials are entirely different chemically from both the natural and the synthetic. These substitutes are made from petroleum oils and contain their lighter fractions. Any substance used in place of natural turpentine, whether it is synthetic or a substitute, should have the following physical properties:

Colorless and lustreless or nearly so.

Solvent and thinning powers for varnish and paint equal turpentine.

Odorless or an odor that is not disagreeable.

Evaporation uniform and not too rapid. It must not begin to distill over 120°C and the upper limit should not be over 180°C

Evaporation residue not over 0.5 per cent.

Flash-point, 30°C or above.

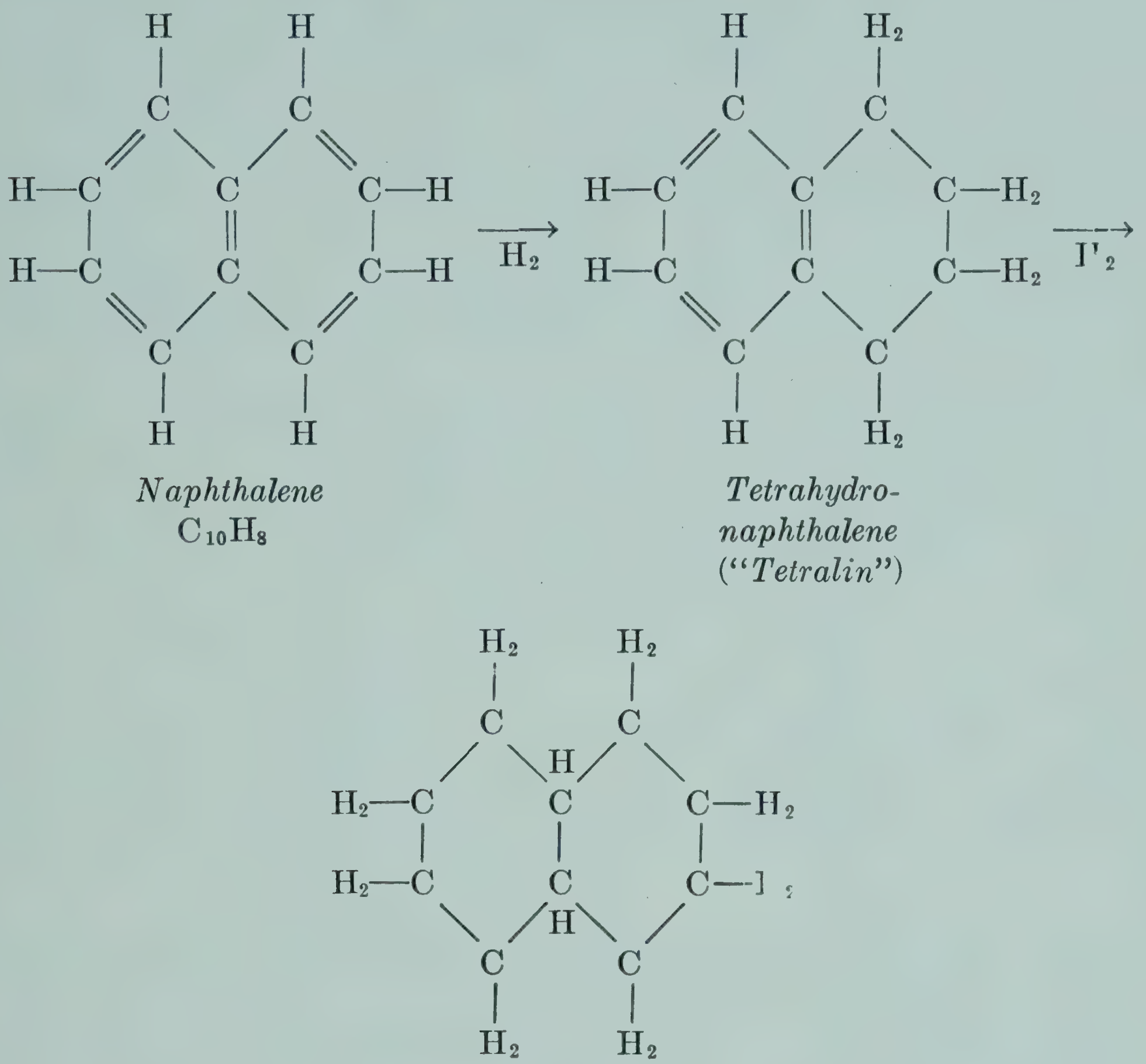
Specific gravity, 0.775 at 15.5° C.

Neutral in chemical reaction.

Clear and free of suspended matter.

One general type of turpentine substitute is made by the hydrogenation of naphthalene, sold under such trade names as "Tetralin" and "Decalin." The former represents the partial hydrogenation and the latter the complete hydrogenation of naphthalene. These do not appear on the market as chemically pure products but contain lower or higher hydrogenated naphthalene.

The petroleum fraction boiling between 150° and 170° C consisting chiefly of nonanes and decanes is being sold as a turpentine substitute. Other mineral spirits of this same type are made by the special oxidation or distillation of petroleum, gas and tar oils. Some of the other products in this group of substitutes are benzine, benzene and its homologs, solvent naphtha, heavy benzol, and white spirits. British Patent 6643 speaks of a turpentine substitute obtained by the oxidation of petroleum oil with picric



Naphthalene
$C_{10}H_8$

Tetrahydronaphthalene
(*"Tetralin"*)

Decahydronaphthalene
(*"Decalin"*)

acid. The resulting product is then subjected to distillation at a temperature between 200° and 250° C. Another process [British Patent 273,832] treats olefinic material with ozone or ozonized air at about 35° C. below the boiling point of the material. The substance obtained is suitable as a turpentine or linseed oil substitute to be used in paint.

Following is a list of the various key patents on turpentine substitutes made from a petroleum base.

French Patent 354,425. 60 parts of petroleum oil and 40 parts terebinthine are mixed and rectified over lime.

U. S. Patent 1,543,570. Refined petroleum is treated with calcium carbide and an alkali. Pine oil is added to the finished product.

British Patent 126,089. 100 parts of petroleum, 3 parts of soda, and 300 parts of water are distilled at 95° to 110°C.

U. S. Patent 1,572,902. An acidulated mixture of resin and naphtha is distilled.

British Patent 1927. A petroleum distillate.

French Patent 661,183. Benzine and sulfur chloride are mixed and agitated. Calcium chloride or an alkali or alkaline earth hypochloride may be added at the same time.

Danish Patent 2219. Petroleum is distilled with a suitable alkali or an alkaline salt. This method serves to separate out the heavy oils.

Chemical Abstracts, page 1,346. Distillation of light oils from Russian petroleum.

Other products resembling turpentine which find their way into commercial channels are vegetable compounds similar to the terpenes. They are made by the oxidation, dehydration or special distillation of pine oil, rosin oil, pine needle oil, or other members of the terpene group of chemicals. Some are known as "wood turpentine," "sulfite turpentine," "Turpenteen," "Terpentix," "Pinex terpentinol," "Teropine," and "Sangojol." "Recovered turpentine" and "regenerated turpentine" are names applied to mixtures of terpenes, often having a peculiar camphor-like odor. These are used as synthetic turpentine and are obtained as by-product in the manufacture of bornyl chloride and synthetic camphor. Superturpentine is a spirit of turpentine rectified below 160°C. This eliminates all constituents other than pinene. "Sangojol," sometimes known as crude Borneo naphtha, is a Borneo petroleum distillate containing cyclic hydrocarbons.

Following are some of the basic patents on synthetic turpentine made from terpene chemicals indicating the character and sources of these materials:

U. S. Patent 1,572,766. Gum of pine, Canada balsam or Peruvian balsam is mixed with 1 to 5 per cent H_3PO_4 and distilled at 310°C.

British Patent 27,024. Pine oil, resin oil or resin spirit containing 1 per cent acetic acid are steam distilled.

French Patent 394,467. Pine oil containing 1 per cent acetic acid or resin acid is heated under 5 atmospheres of pressure in the presence of moist ozone. Then 65 per cent of slake lime is added and the mixture distilled.

U. S. Patent 1,463,122. Pine oil is fractionally distilled between the temperatures 225°C. and 350°C. In the process of distillation the vapors are subjected to the action of a catalyst such as cuprous chloride, cupric chloride, aluminum chloride, hydrochloric acid, or other metal chloride.

U. S. Patent 1,772,895. Pine oil is subjected to distillation in the presence of a contact catalyst (Fuller's earth) at a temperature of about 225° C. Instead of argillaceous earth such as Fuller's earth, silicious earth such as kieselguhr may be used. Activated carbon may be used.

French Patent 400,180. Rosin oil is heated at 400° C. for 5 minutes in the presence of an alkali, then distilled with 0.5 per cent lye.

U. S. Patent 1,691,066. A mixture of pine oil and a halogen is subjected to slow steam distillation. The halogen may be iodine, chlorine or bromine. In addition to a turpentine substitute there is also formed borneol. The substitute has a specific gravity of 0.85 to 0.86, refractive index 1.475 to 1.477 at 20°C., initial boiling point 170°C., and 75 per cent will distill below 185°C.

Another substitute is made by distilling colophony at 270°C. in a vacuum.

U. S. Patent 1,593,030. 1,000 gallons of pine oil, and 50 pounds each of phosphoric acid (85%) and sulfuric acid (66° Bé.) are mixed and heated to 120°C. for two hours. Often this reaction water is drawn off from the bottom of the container. The acid in contact with pine oil is neutralized with soda ash. The altered pine oil is then fractionally distilled. In place of the above acids other dehydrating materials may be used such as zinc chloride, iron chloride and aluminum chloride. The physical properties of the resulting turpentine are as follows: specific gravity 0.8620 to 0.8640 at 15.5°C., refractive index 1.4668 to 1.4673 at 20.0°C., initial boiling point 150° to 154°C., 90 per cent will distill below 170°C., polymerization residue 2 to 3 per cent, flash-point 34 to 35°C., and water-white in color.

German Patent 3420. 100 pounds of colophony, 20 pounds of soda and 50 of water are boiled together, and then mixed with 250 pounds of water and 24 pounds of ammonia. The resulting product is a substitute for turpentine or linseed oil.

Colledge[14] is of the opinion that destructively distilled wood turpentine is superior to all other terpenes for use in the paint and varnish industry. The following is a table of the comparative solvency of some paint and varnish dissolvents as measured by the Kauri-Butanol test.

Lakol	114.8
Turpentine	82.1
Dipentene	105.1
Pine oil	infinite
Gum turpentine	56
Steam distilled turpentine	58
Steam distilled dipentene	60
Steam distilled pine oil	infinite
Toluene	106.7
Xylene	88.2
Solvent naphtha	85.3
Mineral spirit	35.0

Fractions of distillate used in the paint, varnish and lacquer industry are shown in Table 7.14.

Commercial Turpentine[15]

(Typical Properties)

Aniline Point	20.6°C
Distillation range (A.S.T.M.)	
1st Drop	155°C
10%	157.9
30%	158.6
50%	159.1
70%	159.6
90%	162.3
95%	165.5
97%	170.0

TABLE 7.14. TURPENTINES

	SPECIFIC GRAVITY AT 15.5°C	OPTICAL ROTATION	REFRACTIVE INDEX AT 20° C	BOILING POINT (°C)
American turpentine from crude gum of medium quality	0.8670 (20° C.)	−18.8	1.4690	155.0
American turpentine from crude gum of poor quality	0.8695 (20° C.)	−21.6	1.4735	155.5
Newport steam-distilled wood turpentine	0.860–0.864		1.4660–1.4675	154.0
Hercules steam-distilled wood turpentine	0.860–0.866		1.465–1.469	150–158
Aleppe pine oil spirits	0.8543–0.8568	+46.90–46.6	1.4638–1.464	155–158
Algerian turpentine	0.8543–0.8546	+46.2–46.8	1.4636–1.4638	155–156
Austrian turpentine	0.863–0.870	−36° 30′ to −39° 10′	1.46905–1.47033	
French turpentine from crude gum of medium quality	0.8700	−34.1	1.4714	154.8
French turpentine from crude gum of poor quality	0.8730	−34.2	1.4725	154.8
Greek turpentine	0.8605–0.8660	+34–41	1.465–1.474	
Russian turpentine	0.862–0.872	+ 3° to 20°	1.470–1.475	156–171
Sicilian turpentine	0.856–0.863	+25°	1.4464–1.4681	
Spanish turpentine	0.865–0.875	−29 to −23	1.4805	155–156
Venetian turpentine	0.865–0.878	−8° 15′ to −11°	1.46924	

Flash point (Abel Closed Cup)	33.8°C
Kauri-Butanol solvency value	55
Specific gravity at 15.5/15.5°C	0.8613
Optical rotation	+26°C
Refractive index at 20°C	1.4666
Unpolymerized residue (38 NH_2SO_4)	0.6%
Viscosity (Ubbelohde) at 25°C	1.257 cp.

Terpene Solvents. The Naval Stores industry has also responded to the challenge of new solvent expansion. No longer does it restrict itself to turpentine as the only product obtained from the pine tree, but make it yield a wide range of products. The mixtures obtained are separated into their constituent parts by fractional distillation and selective solvent action. Some of these substances are pure anethole, alpha-terpineol, dipentene, alpha-pinene, terpinolene, terpinyl, methyl ester, *p*-cymene and pine oils which range in color from dark to white. The mixtures or impure products are comprised of terpene-alcohol, terpene ketones and hydrocarbons, and moncyclic terpene hydrocarbons. New terpenes (16) have recently been obtained from dead pine wood by solvent extraction. These are dipentene, terpinolene and various terpinenes which are known as "dipentenes". Also cymene has become a recent source of a number of new chemicals which may soon become available in large quantities. These substances are toluic, terephthalic and isopropyl-benzoic acids, dimethyltolylcarbinol *p*-methylstyrene, *p*-methyl-α-methyl-styrene, methylacetophenone and *p*-menthane (17). By rupturing the pinene ring a number of acyclic terpene hydrocarbons[17] are made such as myrcene and ocimene.

Dipentene. The dipentene of commerce is a mixture of the monocyclic terpene hydrocarbons, such as dipentene, terpinolene and the terpinenes. The commercial product, "Solvenol No. 1"[15] is composed principally of dipentene with small amounts of terpinene, terpinolene, cineole, and terpene alcohols. "Dipentene No. 122"[15] is composed mainly of dipentene with small quantities of terpinene and terpinolene. Dipentene is obtained by the fractionation of wood turpentine as well as being a by-product in the manufacture of synthetic camphor. It is a water-white to light straw colored liquid having a pleasant lemon-like odor. It is insoluble in water and methyl alcohol but soluble in ethyl ether, ethyl acetate, acetone, aromatic and aliphatic hydrocarbons, fixed oils, mineral oil, oleic and stearic acids, and most organic solvents.

It is a strong solvent for oleoresinous products, rosin, ester gum, and alkyd resins, waxes, metallic soap driers, and so forth. It is used as a dispersing agent for oils, resins, resin-oil combinations, pigments, and driers, imparting good flow, the retarding of skinning and gelling, and a uniform rate of evaporation which retards initial hardening and exerts leveling action to produce smooth coatings.

TABLE 7.15. SOLUBILITY OF TERPENE SOLVENTS AND SYNTHETIC RESINS[15]

SOLVENT	BAKELITE XR 254	BAKELITE XR 352	BAKE-LITE XR 302	NEVIN-DENE	PARANOL HARD No. 1	PARANOL EX. HARD No. 1	AMBEROL BS-1	REZYL
	(cc. of Varsol required to cause precipitation from 100 cc. of a 50% solution)							
“Solvenol” No. 1	Insol.	10	135	O. K.*	O. K.	O. K.	O. K.	O. K.
Dipentene No. 122†	“	5	80	O.K.	O. K.	O. K.	500	875
“Hercosol” No. 80	40	55	220	O. K.	O. K.	O. K.	O. K.	O. K.
“Hercosol” No. 80‡	140							
“Varsol”	Insol.	Insol.	25	O. K.	O. K.	O. K.	250	875
“Yarmor” pine oil	87	150	350	—	—	—	300	O. K.
P. W. Turpentine	Insol.	Insol.	53	—	—	—	355	O. K.
Pinene No. 111	“	“	57	—	—	—	375	O. K.

* O. K. means a dilution with 1000 cc. of “Varsol” without precipitation.

† Refined Dipentene contains Pinene, Terpinene, Terinolene and Cymene.

‡ Steam-distilled wood turpentine used as diluent.

RESIN	DIPENT-ENE NO. 122	S.D. WOOD TURPENTINES	SOLVENOL NO. 1	HERCO PINE OIL	HER-COSOL NO. 80	PINENE NO. 111	V. M. & P. NAPHTHA
“Dulux” (varnish type)	Sol.	Sol.	Sol.	Sol.	Sol.	Sol.	Partly sol.
“Teglac”	“	Partly sol.	“	“	“	Partly sol.	“ “
“Rezyl” No. 11	“	Insol.	“	“	“	Insol.	Insol.
No. 12	“	“	“	“	“	“	“
No. 17	“	Sol.	“	“	“	Sol.	Partly sol.
Balsam No. 33	“	Insol.	“	“	“	Insol.	Insol.
Balsam No. 53	“	Partly sol.	“	“	“	Partly sol.	“
Kopol No. 9	Sol.	Sol.	Sol.	Sol.	Sol.	Sol.	Insol.
“Bakelite” XR-254	*Insol.	*Insol.	*Insol.	“	“	*Insol.	“
XR-352	Sol.	*Insol.	Sol.	“	“	*Insol.	“
XR-302	“	Sol.	“	“	“	Sol.	Sol.
“Nevindene”	“	“	“	“	“	“	“
Hard No. 1 Paranol	“	“	“	“	“	“	“
Extra-Hard No. 1 Paranol	“	“	“	“	“	“	“
“Amberol” BS-1	“	“	“	“	“	“	“
“Lewisol” No. 2	“	“	“	“	“	“	“

Resin-drying oil combinations soluble in, and solutions capable of dilution with, petroleum thinners. Thinning tolerance of “Solvenol” No. 1 and “Dipentene” No. 122 considerably greater than that of turpentine or pinene.

SOLVENT	RESIN NO. 1†	RESIN NO. 2	RESIN NO. 3	RESIN NO. 4	RESIN NO. 5	RESIN NO. 6	RESIN NO. 7	RESIN NO. 8	RESIN NO. 9
	(cc. of Varsol required to cause precipitation)								
Steam-distilled wood turpentine	30	O. K.	33	O. K.	15	12	6	1	19
"Dipentene No. 122"	38	O. K.	43	O. K.	26	16	10	3	23
"Yarmor" pine oil	115	O. K.	146	O. K.	106	45	38	18	53
"Varsol"	5	140	11	O. K.	7	3	1	Insol.	8

These tests were made by dissolving 10 grams of resin in 10 grams of the solvent named and titrating with Varsol (petroleum thinner) until precipitation of the resin occurred. O. K. signifies no precipitation upon dilution to 4 per cent resin concentration.

SOLVENT	RESIN NO. 5	RESIN NO. 6	RESIN NO. 7	RESIN NO. 8	RESIN NO. 9
	(cc. of solvent required to cause precipitation)				
"Varsol"	18	25	21	Insol.	29
Hercules steam-distilled wood turpentine	O. K.	48	28	26	92
Hercules dipentene No. 122	O. K.	150	63	39	O. K.
"Yarmor" pine oil	O. K.	O. K.	O. K.	O. K.	O. K.

These tests were made by titrating the resin directly with the solvents named.

† Resin No. 1 = Beckacite No. 1100
Resin No. 2 = Beckacite No. 1102
Resin No. 3 = Beckacite No. 1110
Resin No. 4 = Beckacite No. 1112
Resin No. 5 = Beckasol No. 1
Resin No. 6 = No. 1301 P.X. Oil sol.
Resin No. 7 = No. 1304 = A. D.—Oil Solution
Resin No. 8 = No. 1308 = Beck-O-Lac Solution
Resin No. 9 = No. 1310 = A. D. Solution

It is used as a thinner in varnishes and enamels made of synthetic resins, as a wetting agent for enamel pigments, as a solvent in chinawood oil varnishes, as a rubber devulcanizing agent, and as a wetting and dispersing agent in other industries. Having a solvent power similar to that of turpentine, it is used as a substitute for turpentine and petroleum solvents in floor waxes and furniture polish. By adding 15 to 25 per cent of dipentene to petroleum thinners the mixture becomes a solvent for the petroleum-insoluble resinous material. At the same time, should the resinous material be soluble in a petroleum thinner, excellent working qualities and a pleasant odor are imparted by adding 5 per cent dipentene. A 5 to 10 per cent addition of dipentene is recommended for air-drying and baking finishes. The wartime end-use pattern which follows illustrates the principal industrial applications for this solvent.

*Allocations of Dipentene: July 1, 1944–December 31, 1944**

(Thousands of gallons)

Use	Amount	Per cent
Total allocations	1,510	100.0
Export	5	0.3
Other uses	1,505	99.7
Rubber processing	1,074	71.1
Lubricants, cleaners, and carbonizing	154	10.2
Protective coating solvents	149	9.9
Disinfectants, insecticides, and soaps	56	3.7
Textiles	28	1.9
Synthetic resins	25	1.7
Miscellaneous uses and small orders	19	1.2

* "Facts for Industry" Bureau of the Census, Washington, D. C.

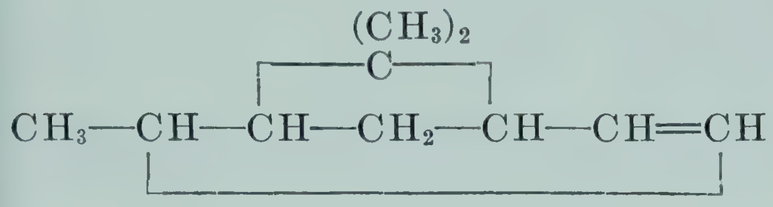
Typical Properties of Dipentene

Distillation range (A.S.T.M.)	
5%	176.0°C
20%	176.5
50%	177.3
70%	178.0
90%	179.0
95%	181.0
97%	188
Fire point	min. 115°F
Flash point (Cleveland open cup)	126°F
Kauri-Butanol value	65
Aniline point	−15°C–6.8°C
Color (Lovibond 500 Amber Series)	1.5
Odor initial	Characteristic
Optical rotation	Approx. +7
Residue	None
Refractive index at 20°C	1.477
Specific gravity at 15.5/15.5°C	0.8518
Water content	None
Weight per gallon	6.42 lbs.

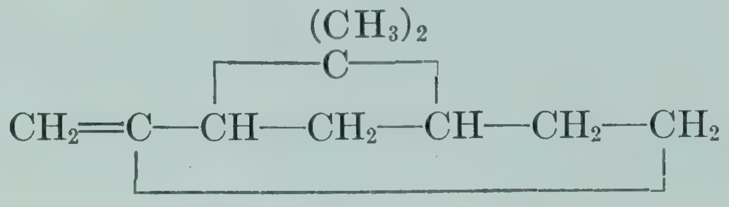
Typical Properties of "Solvenol No. 1"[15]

Distillation range:	
5%	177.0°C
20%	178.6
50%	180.0
70%	181.5
90%	186.0
95%	195.0
Kauri-Butanol solvency value	75
Refractive index at 20°C	1.4770
Specific gravity at 15.5/15.5°C	0.8587
Aniline point	<−15°C
Color (Lovibond 500 Amber Series Glasses)	1.75
Unpolymerized residue	1.6%
Viscosity (Ubbelohde) at 25°C	1.038 cp.

Pinene. Pinene is a water-white liquid with an aromatic odor, containing approximately 96 per cent of *d*-α-pinene. Having a somewhat faster evaporation rate than turpentine, it is used as a thinner for paint, varnishes, and enamels.The presence of pinene in these products gives stability, good flow, and levelling properties.



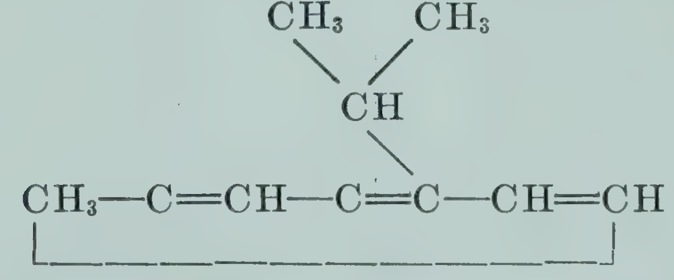
Alpha-Pinene



Beta-Pinene

Distillation range (A.S.T.M.)	
1st Drop	155°C
10%	156.4
30%	156.5
50%	156.6
70%	156.8
90%	157.2
98%	160.0
Kauri-Butanol solvency value	52
Optical rotation	+31
Aniline point	26.2°C
Refractive index at 20°C	1.4665
Specific gravity at 15.5/15.5°C	0.8632
Unpolymerized residue (38 N H_2SO_4)	0.4%
Viscosity (Ubbelohde) at 25°C	1.330 cp.

p-**Cymene** (Cymene, cymol, 1-methyl-4-isopropylbenzene, *p*-cymol)



p-Cymene is made synthetically, and is also obtained as a by-product from sulfite turpentine in the pulping of spruce (17) . It is from this source that it derived such names as "spruce turpentine", "black liquor", and "sulfite turpentine". It is a pleasant-smelling liquid with an odor resembling parsley and soluble in acetone, ethyl alcohol, ethyl ether, chloroform and most other solvents. It is an excellent solvent for oils, fats, resins, hydrocarbons, and many gums. *p*-Cymene is used in lacquer and varnish compositions and when it is added to ethyl alcohol, acetone or *n*-butyl alcohol the resultant mixture is an excellent solvent for paint and varnish, and blends readily with many lacquer solvents. For this reason these mixtures are recommended as paint and varnish removers. It is used in metal

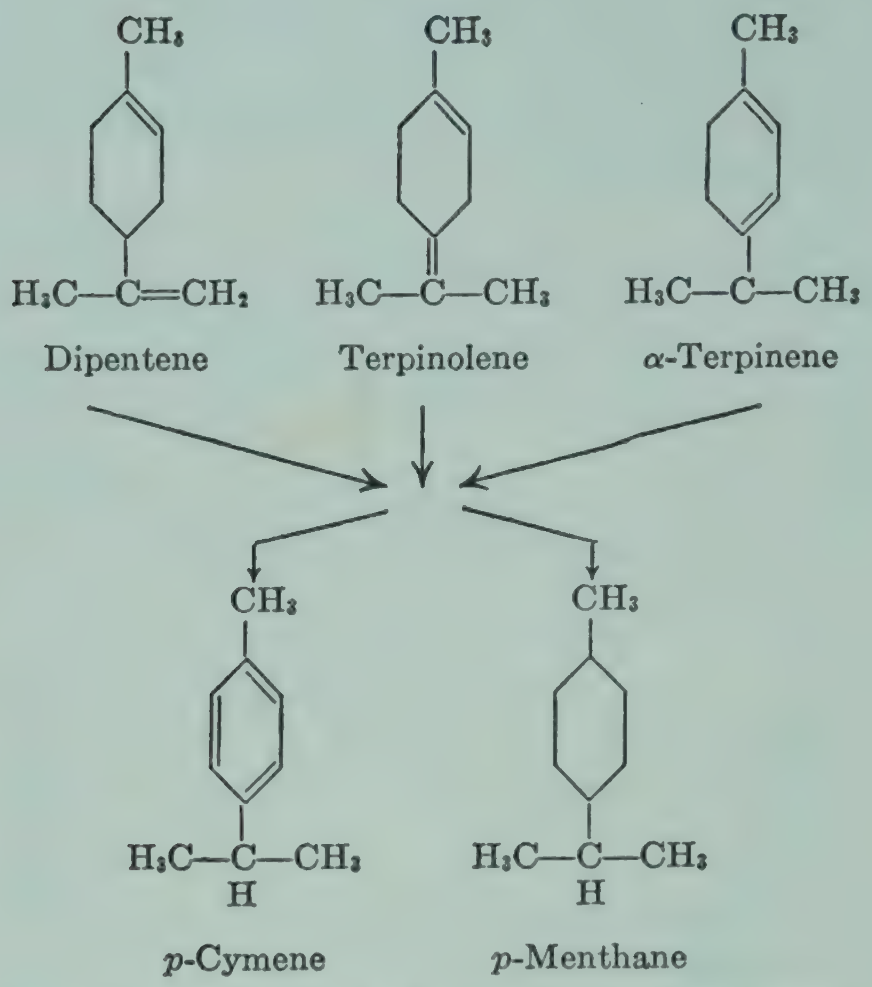

CH₃
H₃C—C=CH₂
Dipentene
CH₃
H₃C—C—CH₃
Terpinolene
CH₃
H₃C—C—CH₃
α-Terpinene
CH₃
H₃C—C—CH₃
H
p-Cymene
CH₃
H₃C—C—CH₃
H
p-Menthane

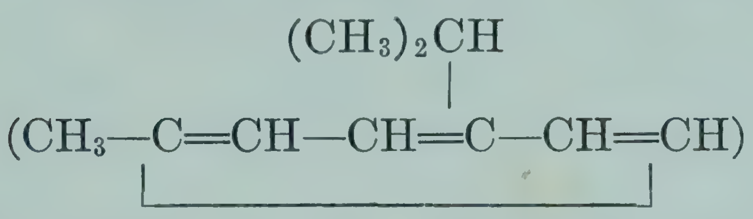
Figure 7.16. Structural Relations of Monocyclic Terpenes with *p*-Cymene and *p*-Methane.

Table 7.16. Solubility of Various Substances in *p*-Cymene

SUBSTANCE	GRAMS IN/100 CC.	TEMP. (°C)
Acetanilide	7.23	30
	1.72	30
	9.24	100
Anthracene	98.60	176
Antipyrine	2.09	30
	0.76	30
Caffeine	15.58	175
deca-Camphoric acid	1.53	100
	2.93	23.5
	16.77	100
Hexachlorobenzene	106.95	176
Naphthalene	14.22	30
β-Naphthylamine	8.63	30
o-Nitroaniline	6.33	30
m-Nitroaniline	1.36	30
p-Nitroaniline	0.83	25
Phloroglucinol	0.12	175
Strychnine	0.71	30

polish, as a substitute for turpentine, and as a starting point for a number of synthetic products.

Boiling range	177–178°C
Specific gravity	0.8612
Melting point	−73.5°C
Refractive index at 20°C	1.4895

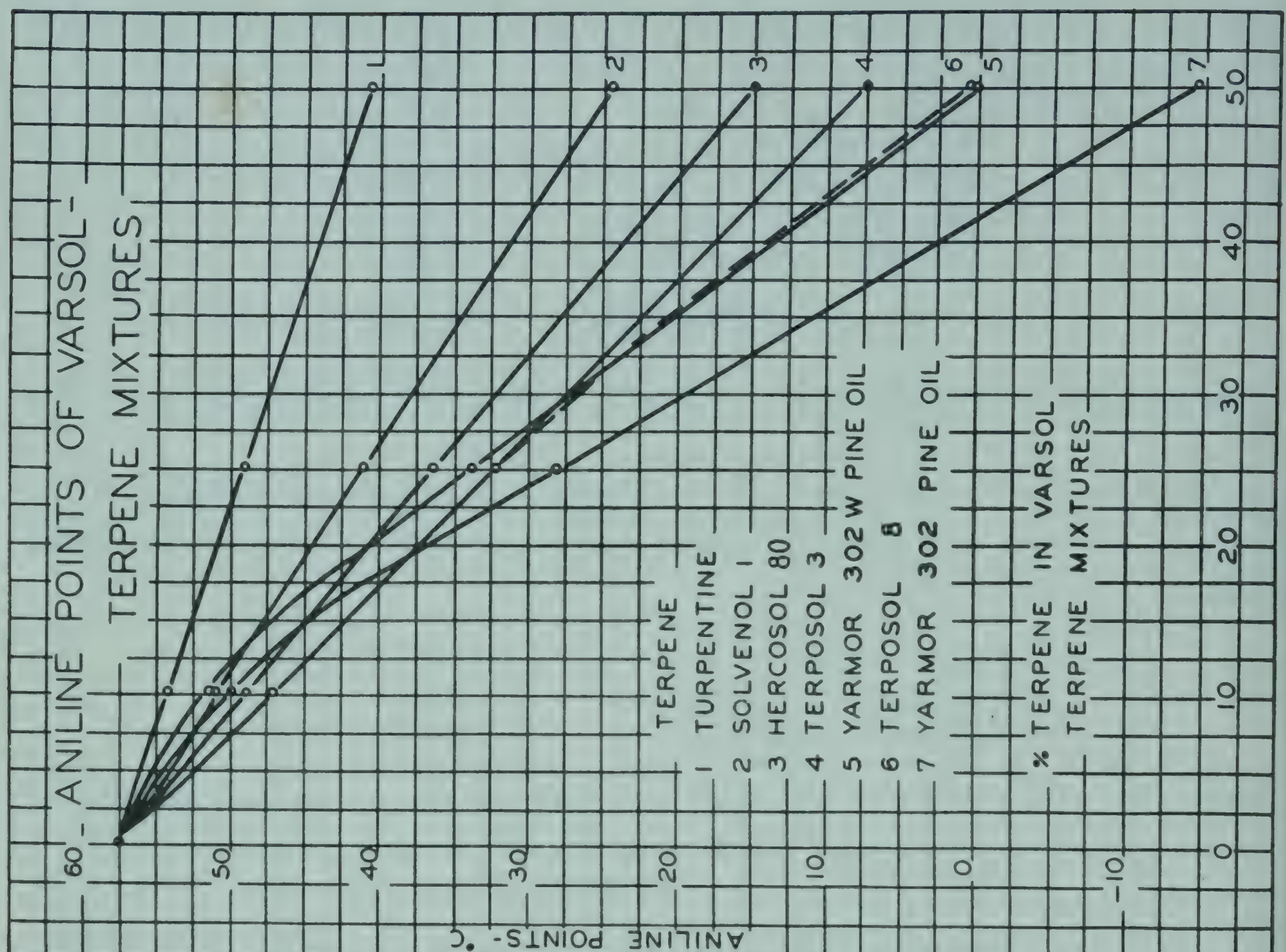
p-**Menthane**  $(\mathrm{CH_3{-}C{=}CH{-}CH{=}\overset{\overset{(CH_3)_2CH}{|}}{C}{-}CH{=}CH})$ *p*-Menthane is made synthetically from dipentene. As a solvent for resins it is inferior to *p*-cymene. It is used in organic synthesis and in solvent mixtures with terpene solvents.

Boiling range	171–172°C
Specific gravity at 15.5/4°C	0.8110
Refractive index at 20°C	1.4420

Pine Oils. Pine oils are obtained by distilling the cones and needles of various species of pine trees, as well as from the stumps of long-leaf yellow pines. Steam-distilled pine oils are obtained by the extraction of chipped pine stumps by means of hot steam and solvents. Destructively distilled pine oil is obtained by distillation of pine stumps with little or no air or oxygen. Pine oil is also made synthetically from turpentine.

Pine oil is miscible with most lacquer solvents and is used as an emulsifying agent, solvent, deodorant, germicide, insecticide and fungicide. It is a source of terpineol, terpene hydrate and fenchyl alcohol and is a denaturant for alcohol. Large quantities of pine oil are used in the ore flotation process, where in dilutions of one part in 150,000 it exerts an affinity for the greasy sulfide particles in a mixture of crushed ore and water. It is used in the separation of metals from gangue, and because of its powerful emulsifying action it is a constituent part of metal polishes, cutting oils, liquid soaps and other types of grease, oil and fat-containing emulsions.

Pine oil soap is composed approximately of 75 per cent soap (50 per cent soap and 50 per cent water) and 25 per cent pine oil. Pine oil soap is transparent and is an excellent emulsifying agent for vegetable and mineral oils. These soaps prohibit the formation of scums and are therefore widely used in laundries, dry-cleaning and in textile processing. Pine oil is of exceptional merit when used in the processing of cotton goods, woolens, worsteds, rayons and silks. Cotton can be washed beautifully white with pine oil soap. Its efficient wetting and penetrating qualities are exhibited by its removal of dirt and waxy material, both rapidly and thoroughly. It also gives level dyeing of good depth on cotton. Its presence also facilitates the washing out of any excess dye. Its dispersing, detergent and neu-


ANILINE POINTS OF VARSOL-TERPENE MIXTURES
ANILINE POINTS - °C
60
50
40
30
20
10
0
-10
0
10
20
30
40
50
TERPENE
1 TURPENTINE
2 SOLVENOL I
3 HERCOSOL 80
4 TERPOSOL 3
5 YARMOR 302 W PINE OIL
6 TERPOSOL 8
7 YARMOR 302 PINE OIL
% TERPENE IN VARSOL TERPENE MIXTURES
1
2
3
4
5
6
7

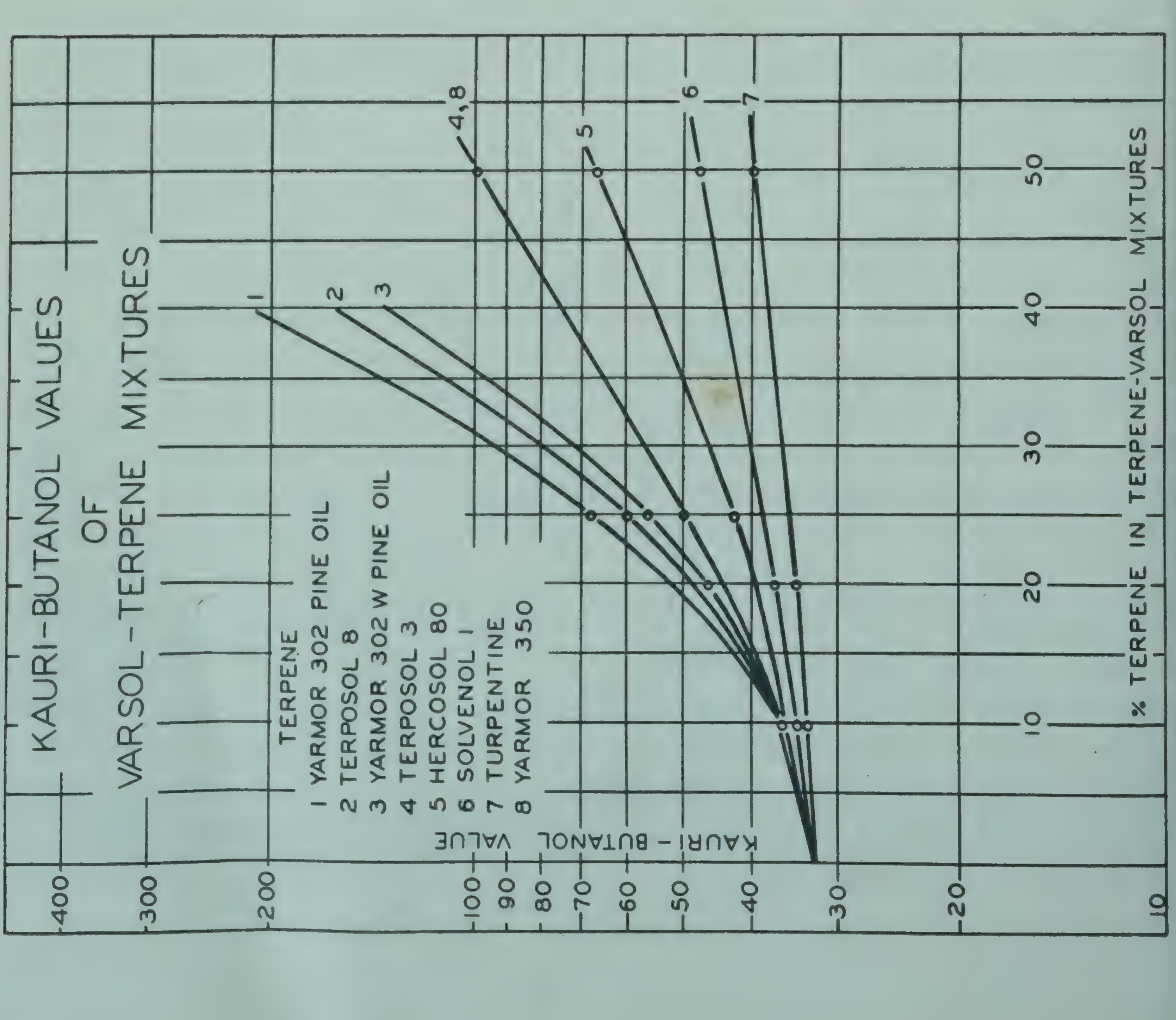

KAURI-BUTANOL VALUES OF VARSOL-TERPENE MIXTURES
KAURI-BUTANOL VALUE
400
300
200
100
90
80
70
60
50
40
30
20
10
TERPENE
1 YARMOR 302 PINE OIL
2 TERPOSOL 8
3 YARMOR 302 W PINE OIL
4 TERPOSOL 3
5 HERCOSOL 80
6 SOLVENOL I
7 TURPENTINE
8 YARMOR 350
% TERPENE IN TERPENE-VARSOL MIXTURES
10
20
30
40
50
1
2
3
4,8
5
6
7
8

Figure 7.18

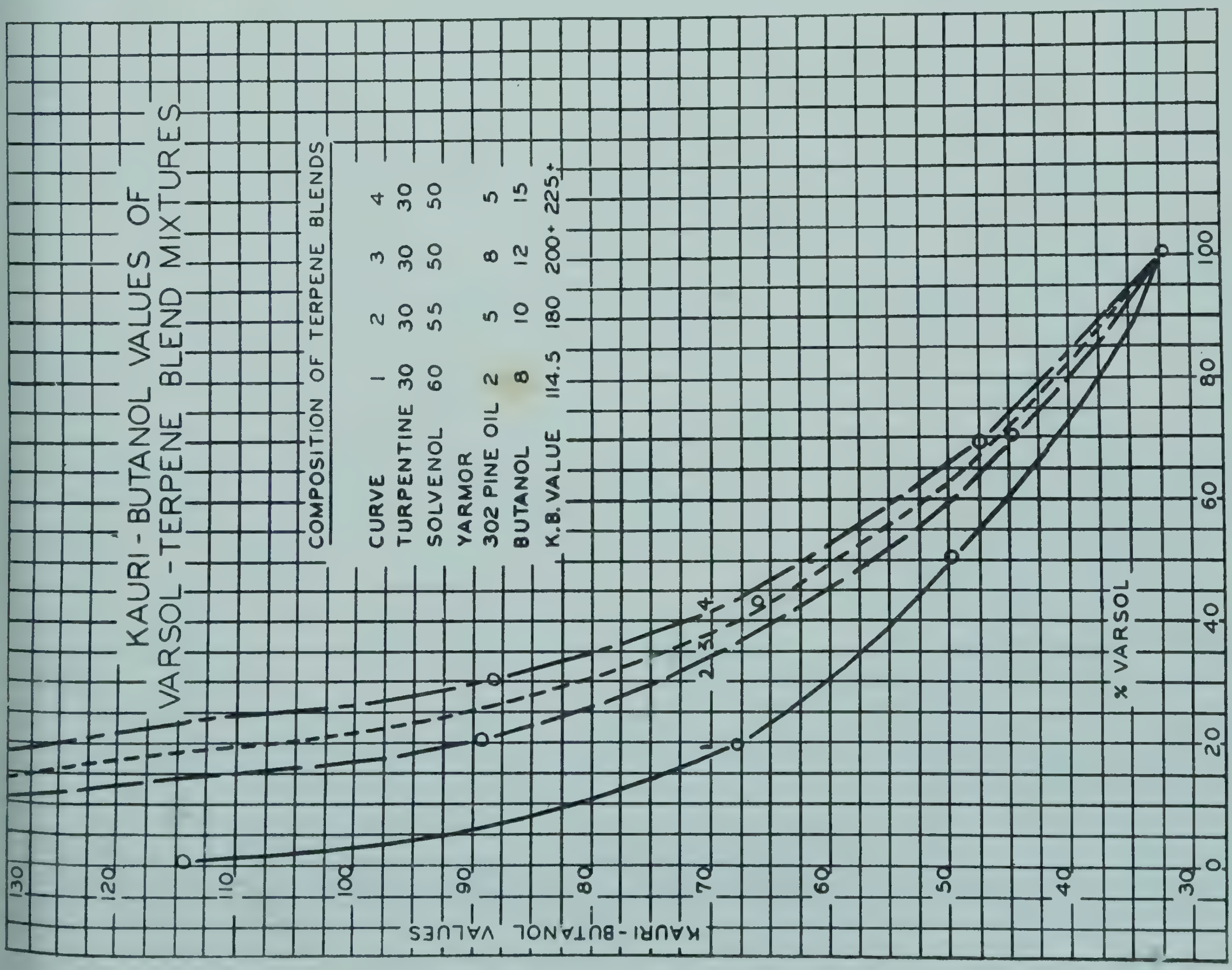


Figure 7.19.

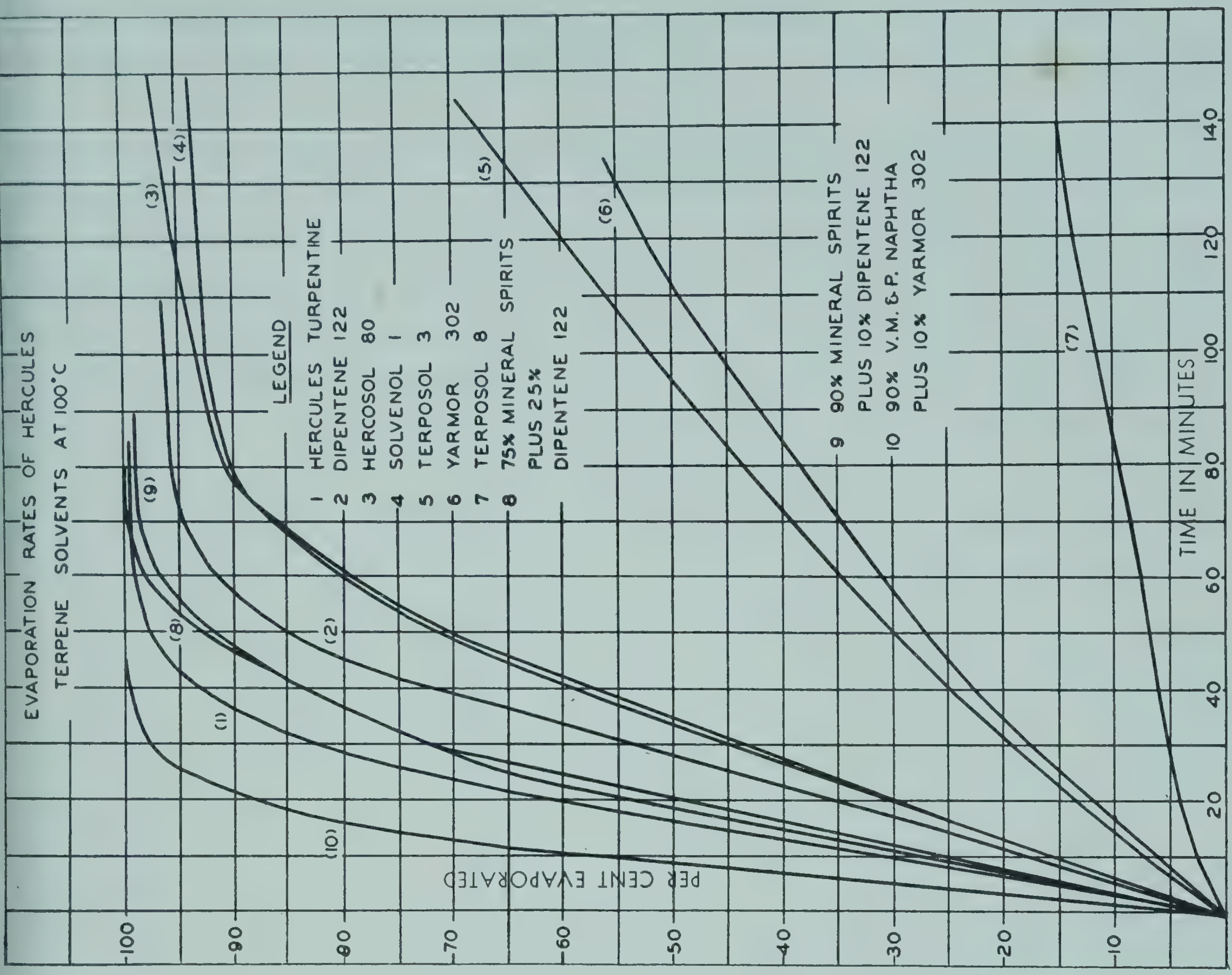


Figure 7.20.

tral properties make it particularly useful in soaps, as a rayon boil-off agent, as a scouring agent for wool, for degumming silk and in dispersing metal soaps.

Pine oil is used in paints and varnishes for its piny odor, solvency, penetration, wetting and good working qualities, and so forth. It is used in dried finishes to the extent of 2 per cent and in baked finishes where no more than 5 per cent is used. The presence of pine oil in varnishes of the phenol-resin type prevents precipitation, gelling and skinning. It is used in ship-bottom and asphalt paints and in prepared waxes; it facilitates pigment grinding and holds powders in suspension.

TABLE 7.17. BLENDED SOLVENTS[15]

COMPOSITION	1	2	3	4
"Yarmor" 302 Pine Oil	2%	5%	8%	5%
"Solvenol No. 1"	60%	55%	50%	50%
Turpentine	30%	30%	30%	30%
Butanol	8%	10%	12%	15%
PROPERTIES				
Kauri-Butanol Value	115	180	200+	200+
Specific Gravity @ 15.5/15.5° C	0.8497	0.8481	0.8518	0.8485
Flash Point (Cleveland Open Cup)	44° C	44.5° C	40.5° C	40.5° C
A.S.T.M. Distillation range: 5%	141.0° C	133.8° C	132.0° C	126.0° C
10%	151.0° C	148.8° C	140.0° C	134.0° C
30%	175.3° C	173.8° C	172.0° C	171.0° C
50%	177.8° C	177.8° C	178.8° C	177.8° C
70%	179.8° C	178.8° C	181.0° C	179.8° C
90%	183.8° C	185.8° C	194.0° C	186.8° C
95%	190.3° C	190.6° C	205.0° C	195.0° C

CHARACTERISTICS OF TERPENE-MINERAL SPIRITS MIXTURES

COMPOSITION	1	2	3	4	SOL-VESSO NO. 3
Blend (from Table I)	90% (1)	75% (2)	70% (3)	66% (4)	
Mineral Spirits	10%	25%	30%	34%	
PROPERTIES					
Kauri-Butanol Value	80	80	82	78.5	73.8
Viscosity of Alkyd @ 40% solids	L M	L—M	L	M	M
Specific Gravity @ 15.5/15.5° C	0.8413	0.8306	0.8374	0.8268	
Flash Point (Cleveland Open Cup)	44.0° C	43.0° C	42.0° C	40.5° C	
A.S.T.M. Distillation Range: 5%	142.0° C	136.0° C	135.0° C	124.0° C	
50%	177.0° C	177.0° C	174.0° C	174.0° C	
95%	190.0° C	190.0° C	190.0° C	188.0° C	

KAURI-BUTANOL SOLVENCY VALUES OF TERPENE-MINERAL SPIRITS MIXTURES

TERPENE	10%	20%	25%	50%	100%
"Yarmor" 302 Pine Oil	36	57	69	300+	500+
302-W Pine Oil	36	50	57	300+	500+
350 Pine Oil	38.7	45.4	49	101	Approx. 500
"Terposol" No. 3	37	—	50	99	Approx. 500
No. 8	40	—	60	300+	500+
"Hercosol" No. 80	36	—	43	66	500+
"Solvenol No. 1"	35	38	—	47	75
Turpentine	33	36	—	41	55
"Dipentene No. 122"	33	—	38	—	62
Mineral Spirits					32

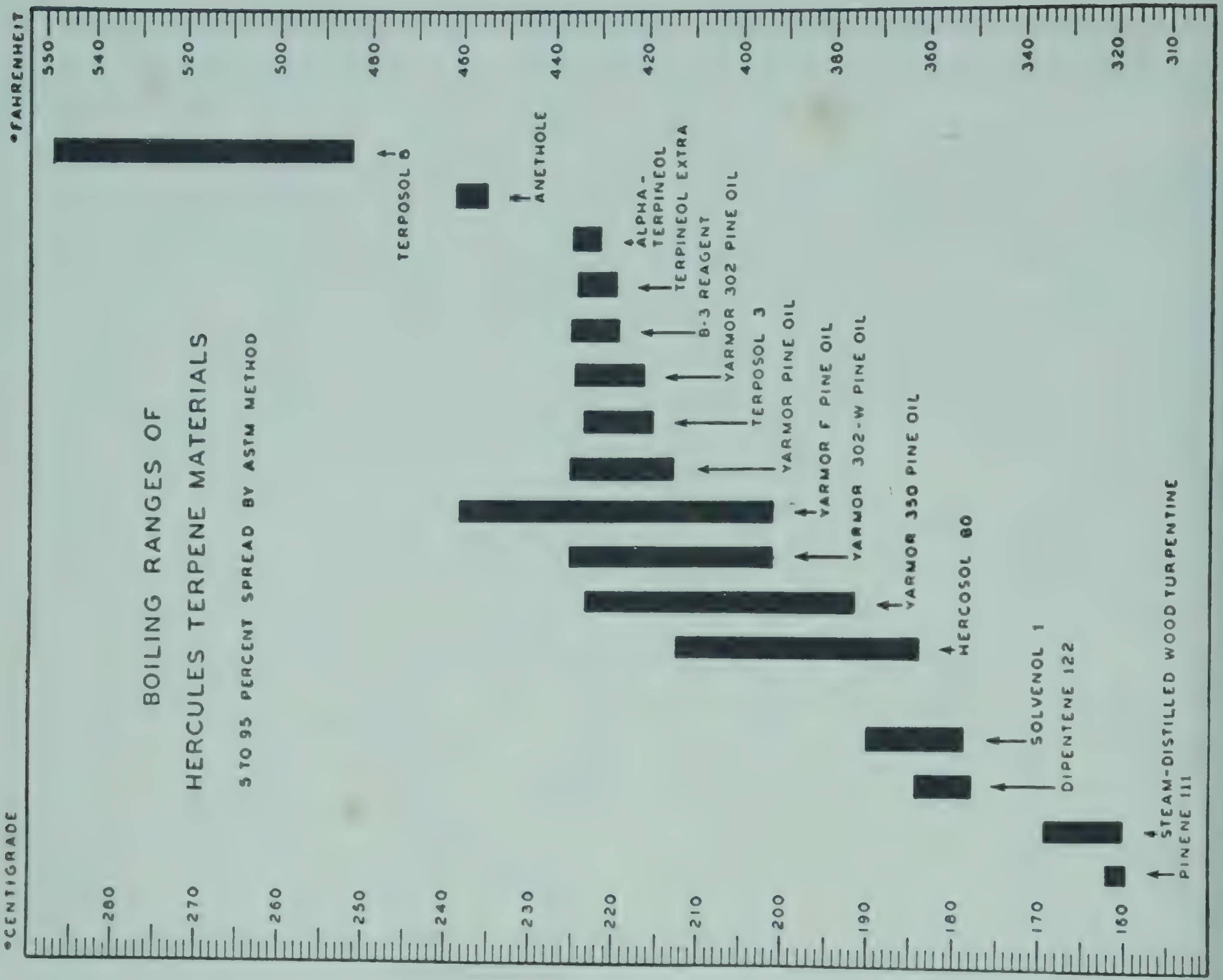
ANILINE POINTS (°C.)

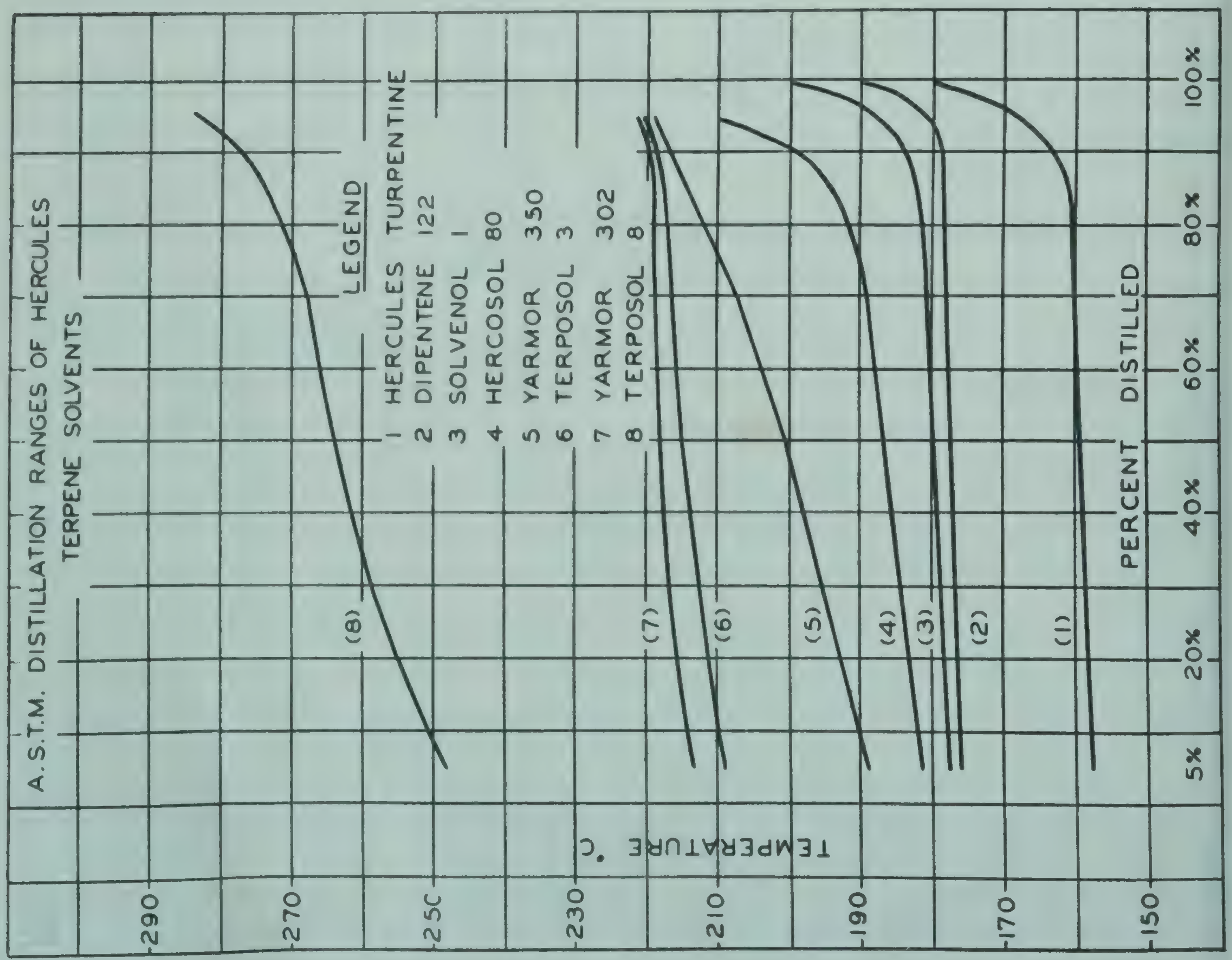
TERPENE	% TERPENE IN MIXTURE				
	10%	20%	25%	50%	100%
"Yarmor" 302 Pine Oil	49°	34°	29°	−14°	<−20°
302-W Pine Oil	51°	46°	33°	0.3°	<−20°
"Terposol" No. 3	47°	—	32°		<−20°
No. 8	47°	—	34°	0.3°	<−20°
"Hercosol" No. 80	46°	—	37°	7.5°	<−15°
"Solvenol No. 1"	50°	44°	—	15°	<−15°
Turpentine	53°	50°	—	25°	20.6°
"Dipentene No. 122"	52.5°	—	45.5°	21°	−6.8°
Mineral Spirits				—	57.5°

VISCOSITY REDUCTION OF ALKYD SOLUTION @ 25% SOLIDS WITH MINERAL SPIRITS-TERPENE MIXTURES

SOLVENT COMPOSITION	VISCOSITY OF ALKYD SOLUTION
100% Mineral Spirits	47.0 cp.
90% Mineral Spirits + 10% Turpentine	39 cp.
90% Mineral Spirits + 10% "Dipentene No. 122"	37 cp.
90% Mineral Spirits + 10% "Solvenol No. 1"	32 cp.
90% Mineral Spirits + 10% "Yarmor" 302 Pine Oil	17 cp.
90% Mineral Spirits + 10% 350 Pine Oil	22 cp.
90% Mineral Spirits + 10% "Terposol" No. 3	25 cp.
90% Mineral Spirits + 10% No. 8	21 cp.
90% Mineral Spirits + 10% "Hercosol" No. 80	28 cp.

Although pine oil is nontoxic and noncaustic, it exhibits disinfectant and insecticidal properties. The following formula is shown to possess a phenol coefficient of 5 (*B. typhosus*, modified Rideal-Walker test): pine oil $62\frac{1}{2}\%$, rosin soap and water $37\frac{1}{2}\%$. It has been proved that when pine oil


BOILING RANGES OF
HERCULES TERPENE MATERIALS
5 TO 95 PERCENT SPREAD BY ASTM METHOD
°FAHRENHEIT
550
540
520
500
480
460
440
420
400
380
360
340
320
310
°CENTIGRADE
280
270
260
250
240
230
220
210
200
190
180
170
160
TERPOSOL 8
ANETHOLE
ALPHA-TERPINEOL
TERPINEOL EXTRA
B-3 REAGENT
YARMOR 302 PINE OIL
TERPOSOL 3
YARMOR PINE OIL
YARMOR F PINE OIL
YARMOR 302-W PINE OIL
YARMOR 350 PINE OIL
HERCOSOL 80
SOLVENOL 1
DIPENTENE 122
STEAM-DISTILLED WOOD TURPENTINE
PINENE 111


A.S.T.M. DISTILLATION RANGES OF HERCULES
TERPENE SOLVENTS
LEGEND
1 HERCULES TURPENTINE
2 DIPENTENE 122
3 SOLVENOL 1
4 HERCOSOL 80
5 YARMOR 350
6 TERPOSOL 3
7 YARMOR 302
8 TERPOSOL 8
(1)
(2)
(3)
(4)
(5)
(6)
(7)
(8)
TEMPERATURE °C
290
270
250
230
210
190
170
150
PERCENT DISTILLED
5%
20%
40%
60%
80%
100%

is used in proper dilution it will kill many types of pathogenic organisms and will repel many insects. Pine oil has definitely valuable fungicidal action against organisms causing ringworm.

Pine oil has been converted into mixtures of terpene hydrocarbons and ketones of lower specific gravity and volatility which evaporate more rapidly and are less hygroscopic. These new close-cut, lower-boiling fractions are making inroads as solvents for gums and resins such as copal and dammar, ester gum, kauri, manila, metallic soaps, cellulose ethers, and so forth. The solvency of these pine oils is greatly improved when they are mixed with alcohols. These blends are used in dipping and brushing lacquers, in wire-coating enamels, in quick-drying and baking enamels and in alkyd varnishes. Solvent mixtures containing these pine products improve gloss, flow, levelling and wetting properties, and tend to prevent blushing, skinning and rapid surface drying. They are used in reclaiming rubber, as wetting agents in grinding liquids and as mutual solvents for linseed oil, turpentine, oil varnishes, nitrocellulose lacquers and spirit varnishes.

Properties of Natural Pine Oil

	Heavy white	Water white
Acidity (as acetic acid)	0.07%	0.07%
Color	Light straw to white	
Distillation range		
5%	214°C	195°C
50%	217	212
90%	218	218
95%	222	220
Specific gravity at 15.5°C	0.945	0.932
Fire point (Tag Open Cup)	204°F	178°F
Flash point (Tag Open Cup)	188°F	163°F
Index of polymerization residue	1.500	1.500
Kauri-Butanol value	Infinity	
Odor initial	Characteristic	
Residue unpolymerized	2.5%	2.5%
Refractive index at 20°C	1.4835	1.4810
Water content	0.3%	0.25%
Weight per gallon at 60°F	7.74 lbs.	7.81 lbs.

Properties of Synthetic Pine Oil

Color Lovibond 500 Amber Series	1.25	3.0
200 Red Series	0.25	
Distillation range (A.S.T.M.)		
5%	196.0°C	198.2°C
30%	204.0	205.2
50%	210.0	210.2
70%	216.0	215.2
95%	222.0	222.2

Specific gravity at 15.6/15.6°C	0.9180	0.9214
Flash point	150.0°F	166.0°F
Freezing point	Below—10.0°C	Below—10.0°C
Moisture	0.25%	0.2%
Refractive Index at 20.0°C	1.4815	1.4792
Specific rotation	+4.0°	+5.2°
Unpolymerized residue	0.4%	0.4%

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Chapter 8

Halogenated Hydrocarbons

ALIPHATIC

As mentioned in Chapter 6, the introduction of halogenated aliphatic and aromatic hydrocarbons has helped to reduce the fire hazard associated with the use of solvents in industry. These solvents have consequently found wide application in dry cleaning, metal degreasing, extraction processes, and to a lesser extent in paint and varnish manufacture. Their low flammability is utilized to raise the flash point of highly volatile solvents. For example, the flammability of acetone can be substantially decreased by the addition of carbon tetrachloride. The halogenated hydrocarbons are miscible with most organic solvents and are equally good solvents for oils, fats, resins, waxes, asphalt, rubber, gutta percha, and sulfur. Their specific gravities range from 1.68 to 2.97 and these high densities are of distinct advantage in keeping bronze powder and heavy pigments in suspension.

The lower-boiling alkyl and aryl halides generally have a low heat of vaporization and narrow distillation range, thus producing rapid and complete evaporation—a factor of importance in extraction processes. The chlorinated hydrocarbons are fairly stable, although some of them show a tendency to hydrolyze in the presence of moisture, air, heat, or light.

Methyl Bromide (Monobromomethane) CH_3Br. Monobromomethane is a gas boiling at 4.6°C; it is nonflammable and has a sweet odor. It is miscible with alcohols, ethers, ketones, esters and halogenated hydrocarbons but is soluble in water only to the extent of 0.097 per cent by weight. It is used as a refrigerant, as a low-boiling solvent, and in organic synthesis.

Boiling point (760 mm)	4.6°C
Melting point	−84°C
Critical temperature	173.3°C
Dielectric constant at 100°C	0.0068
Flash point	None
Freezing point	−93°C
Heat capacity	1.27 (16°C) (0.3–0.6 atm.)
Heat of combustion	184 kg. cal./mol.
Purity	99.8%
Specific gravity at 0/0°C	1.732
Thermal conductivity at 0°C	0.574

Vapor pressure at −30°C	130 mm
−10	380
4.6	760
10	890
20	1250
30	1800
40	2300
Weight per gallon at 0°C	14.4 lbs.

Methyl Chloride (CH_3Cl). Methyl chloride was discovered by Dumas and Peligot[1] as early as 1835. Until recent years it had only limited production, but this changed in 1920 when it began to be produced in commercial quantites to supply the increased demands for refrigerants. Methyl chloride is a colorless gas when at room temperature and atmospheric pressure, with a nonirritating, ethereal odor. It is a stable and noncorrosive compound when in a dry state, but slowly decomposes in the presence of water to hydrochloric acid, thus becoming corrosive to metals. It must not be placed in contact with aluminum, since it forms a spontaneously flammable methyl aluminum compound. It is readily soluble in alcohol, mineral oils, chloroform, and most organic liquids. It is insoluble in water.

It is used as a refrigerant; as a catalyst; as a solvent in the manufacture of certain synthetic rubbers; for resins, insecticides, and fungicides applied by the aerosol technique; as a dewaxing agent in the refining of petroleum products; as a solvent in low-temperature extraction of greases and essential oils; and in organic synthesis.

Goodhue[2] experimented with methyl chloride as an insecticidal spray by dissolving it in 5 per cent by weight of purified pyrethrum extract (containing 20 per cent total pyrethrum) and 2 per cent by weight of sesame oil. Methyl chloride will also dissolve nicotine, rotenone, thiocyanates, and many other insecticides.

Typical Properties and Specifications

Boiling point (760 mm)	−23.8°C
Coefficient of cubical expansion Average/°C Liquid 0°–40°C	0.0022
Critical pressure (65.9 atm)	968.7 lb./sq. in absolute
Critical temperature	289.4°F
Explosive limits in air	8.1% to 17.2% by vol.
Flash point	Below 0°C
Freezing point	−97.6°C
Solubility in cc of gas in 100 cc solvent at 20°C (760 mm)	
Water	303
Benzene	4723
Carbon tetrachloride	3756
Glacial acetic acid	3679
Ethyl alcohol	3740

TABLE 8.1. VAPOR PRESSURE, DENSITY, AND HEAT CONTENT OF LIQUID METHYL CHLORIDE

TEMP. °F.	PRESSURE		DENSITY		HEAT CONTENT ABOVE −40°		
	Abs.	Gage	Liquid	Saturated vapor	Liquid	Latent	Vapor
	Lb./sq. in.		Lb./cu. ft.		B.t.u./lb.		
−40	7.40	14.86[a]	64.39	0.0766	0	0.4540	0.4540
−30	9.40	10.79[a]	63.82	0.0990	0.0080	0.4386	0.4466
−20	11.78	5.94[a]	63.21	0.1240	0.0160	0.4237	0.4397
−10	14.90	0.20	62.62	0.1550	0.0240	0.4093	0.4333
0	18.70	4.00	61.99	0.1930	0.0320	0.3955	0.4275
10	23.26	8.56	61.35	0.2390	0.0400	0.3822	0.4222
20	28.76	14.06	60.68	0.2920	0.0480	0.3694	0.4174
30	35.19	20.49	60.06	0.3560	0.0556	0.3570	0.4126
32	36.57	21.87	59.92	0.3716	0.0570	0.3546	0.4116
40	42.61	27.91	59.42	0.4320	0.0630	0.3449	0.4079
50	51.52	36.82	58.75	0.5203	0.0705	0.3332	0.4037
60	61.74	47.04	58.11	0.6290	0.0779	0.3216	0.3995
70	73.40	58.70	57.44	0.7410	0.0852	0.3105	0.3957
80	86.72	72.02	56.72	0.8770	0.0924	0.2996	0.3920
90	101.99	87.29	56.02	1.017	0.0994	0.2891	0.3885
100	119.04	104.34	55.34	1.181	0.1064	0.2789	0.3853
110	137.20	122.50	54.59	1.319	0.1134	0.2688	0.3822
120	155.80	141.10	53.71	1.495	0.1204	0.2586	0.3790
130	176.30	161.60	52.80	1.695	0.1274	0.2481	0.3755
140	200.00	185.30	51.81	1.905	0.1336	0.2362	0.3698

[a] Indicates inches of vacuum.

Latent heat of evaporation at B.P.	102.4 cal./g.
Specific gravity at 20.7°C/4°C	1.002
Specific heat at 20°C (liquid)	0.382 cal./g./°C
Solubility in water at 25°C	0.48 g./100 g.
Solubility of water in Solvent at 10.76°F	0.026% by wt.
Solubility in glycerin at 77°F	0.3% by wt.
Solubility of glycerin in methyl chloride at 77°F	0.03% by wt.
Vapor density at B.P. (760 mm)	2.47 g./liter
Water content	008% by wt., maximum
Weight per gallon at −23.7°C	8.34 lbs.
Acidity as HCl	0.001% by wt., maximum
Boiling range (760 mm)	−24.6 to −23.6°C
Melting point	−144°F
Odor initial	Faintly sweet, ethereal
Purity	Not less than 99%
Residue on evaporation	0.01% by wt., maximum

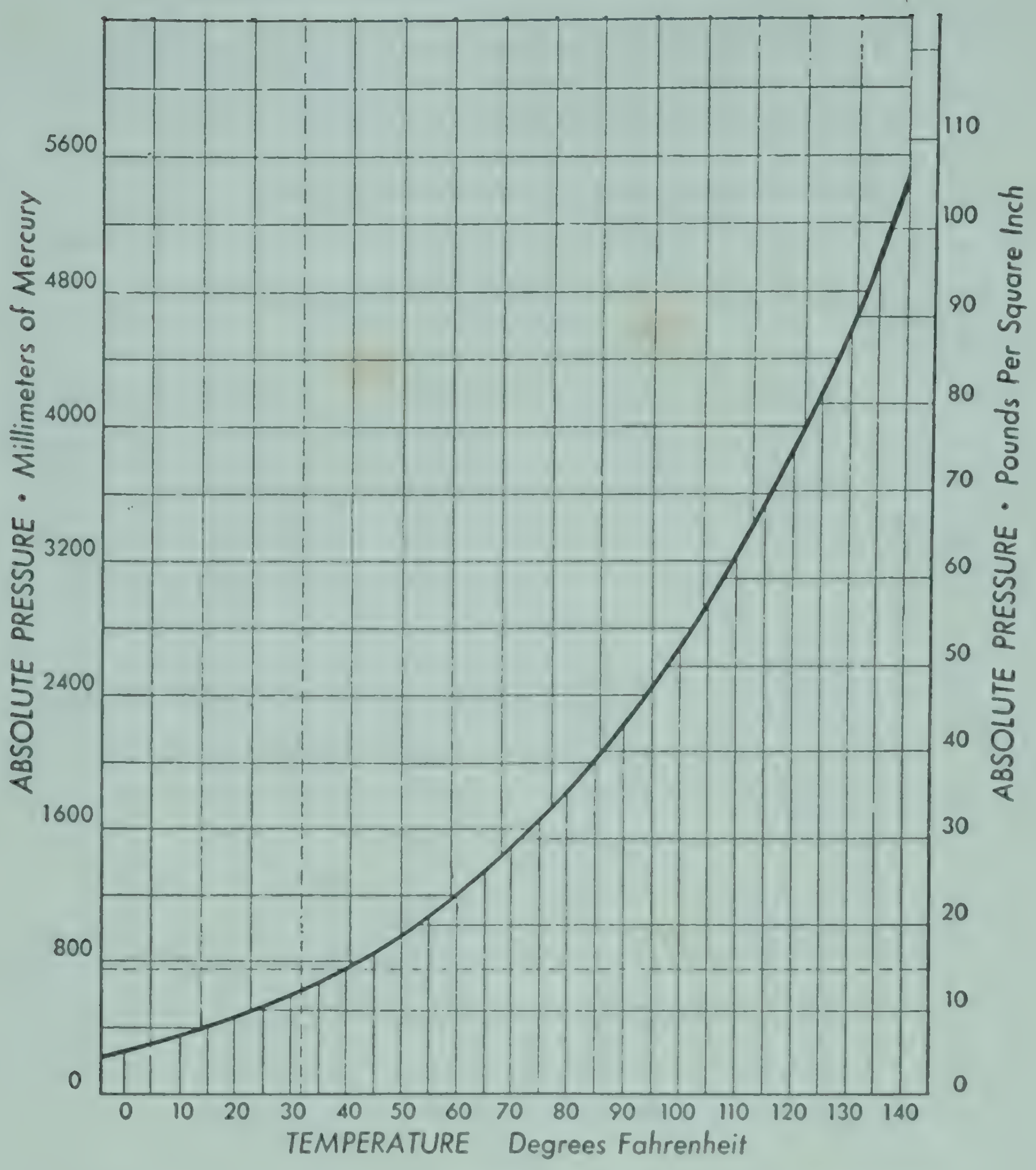


Figure 8.1. Vapor Pressures of Methyl Bromide.

Volume of Methyl Chloride

°F.	%
60	100.0
80	102.4
100	105.0
120	108.2
140	112.1

Dichloromethane (Methylene chloride, methylene dichloride) (CH_2Cl_2). Methylene dichloride is a colorless, heavy, mobile, and low-boiling liquid with a pleasant ethereal odor. It is made by the chlorination of methane and frequently contains traces of methyl chloride and chloroform. This solvent is miscible in all proportions with alcohol, ether, and chloroform and is only slightly soluble in water. It is miscible with many lacquer solvents and is a solvent for cellulose esters and ethers, having increased solvent power when mixed with an alcohol, ether or ester for alkaloids, bitumens, rubber, oils, resins, waxes, and many other organic compounds. It is used as a solvent in textile and leather coatings, where its low boiling point and quick evaporation make it especially suitable. As a low-boiling solvent it is also useful in the manufacture of artificial leather, cellulose acetate, and in films.

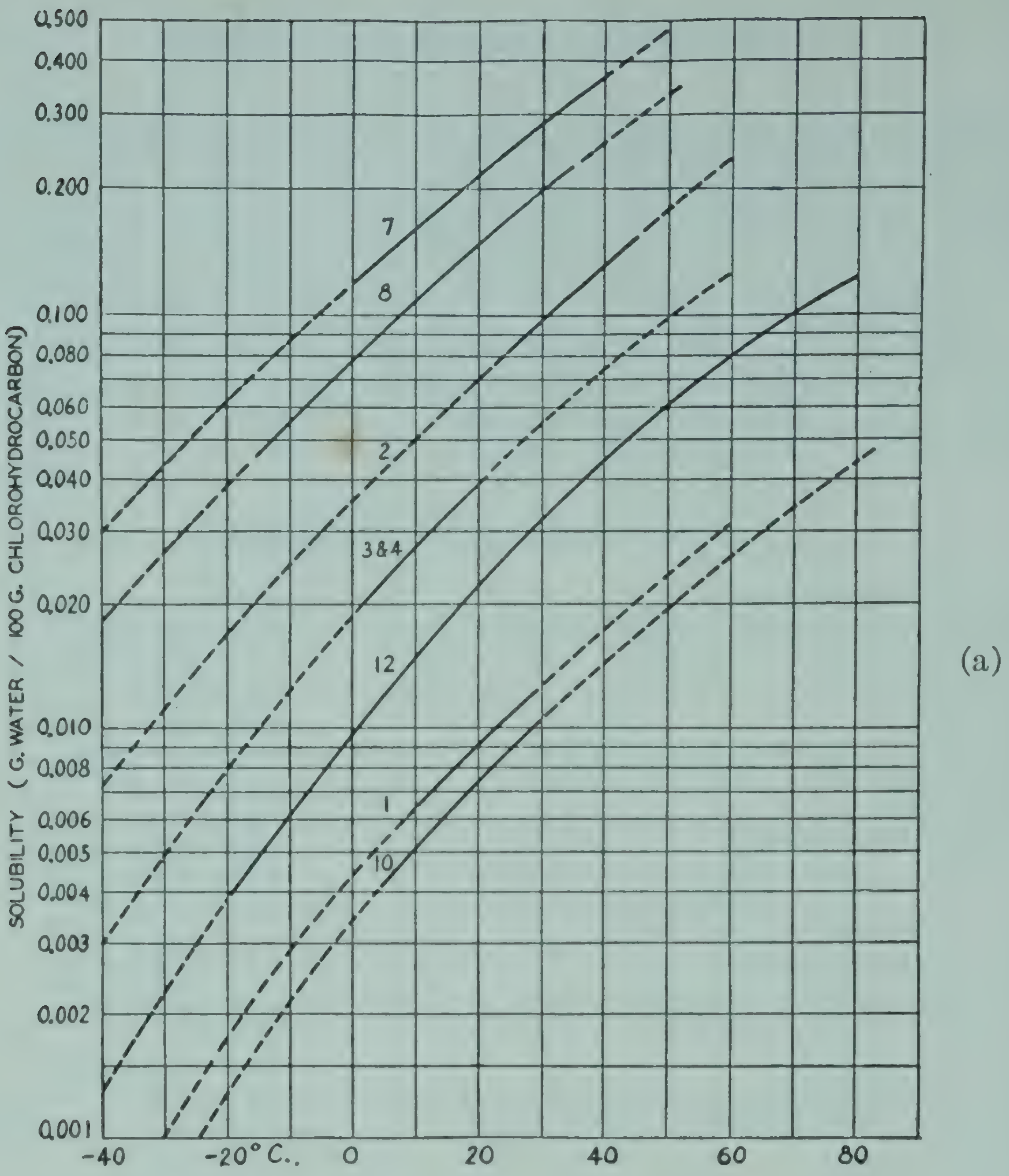
Methylene dichloride finds application in fire-extinguishing compositions; in the preparation of hexamethylenetetramine; as a refrigerant in low-pressure ice machines and air-conditioning apparatus; as a local anesthetic in dentistry; and in the extraction of oils, fats, perfumes, flavors, and drugs. It also is used as a spotting agent, a degreasing medium, in the dewaxing of lubricating oils, and as an intermediate in the manufacture of synthetic dyes, drugs, and perfumes.

Typical Properties and Specifications

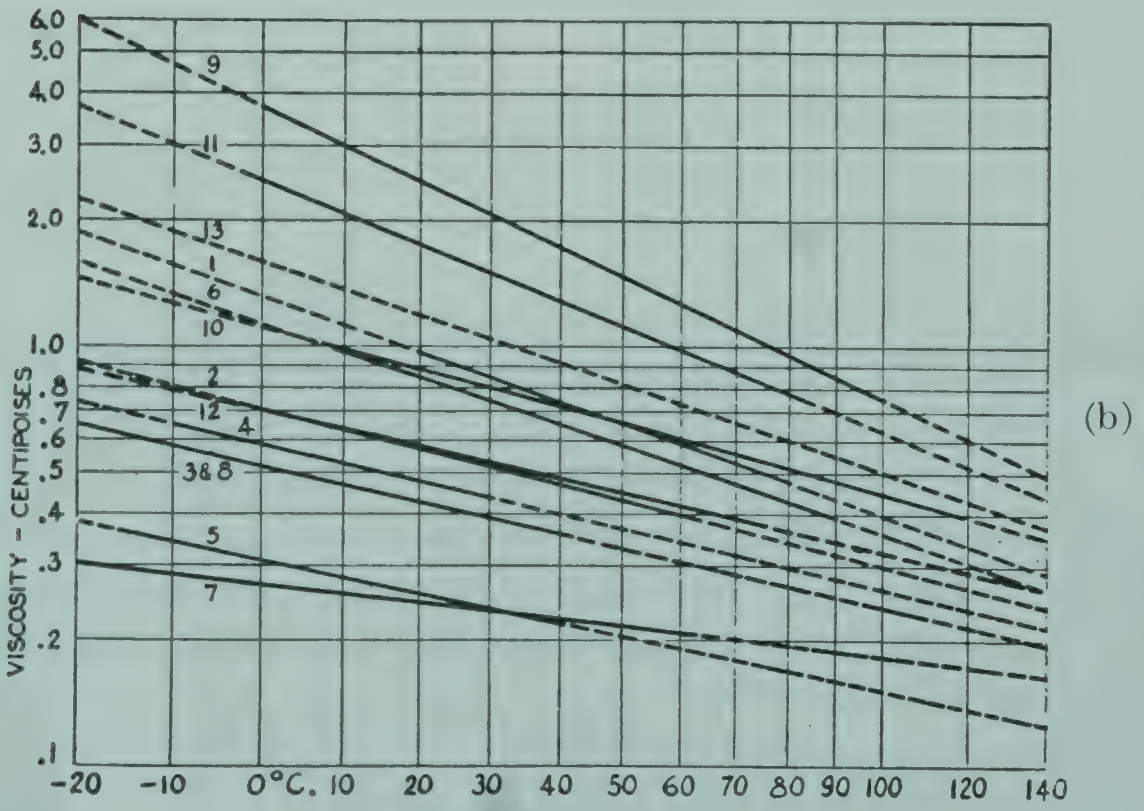
Boiling Point at 760 mm	39.8°C
Coefficient of Cubical Expansion Av./°C Liquid	0.00136 0–40°C
Dielectric Constant	1.17 at 60–140°C
Freezing Point	−96.7°C
Latent Heat of Evaporation at B.P.	78.74 cal./gm.
Refractive index	1.4237
Specific gravity at 15/4°C	1.333–1.336
Specific heat at 20°C (Liquid)	0.284 cal./g./°C
Surface tension against air (18°C)	26.52 dynes/cm.
Solubility in water at 25°C	2.11 g./100 g.
Vapor density (at B.P. and 760 mm)	3.32 g./liter
Vapor pressure at 30°C	530 mm
Viscosity liquid at 20°C	0.441 centipoises
Water content: no cloud at −40°C	0.02% by wt., maximum
Weight per gallon	11.13 lbs.
Acidity	Less than 0.001% calculated as HCl
Boiling Range at 760 mm	39.2–40.0°C
Color	Water-white, not darker than Saybolt 24
Free Halogens	None
Odor Initial	No foreign odor
Residue	Not over 0.00075% by wt.

Chloroform (Trichloromethane) ($CHCl_3$). Chloroform is a heavy, water-white, volatile, and highly anesthetic liquid having a sweet odor. In the absence of water it is a stable liquid. It is only slightly soluble in water, but is soluble in ethyl alcohol, ethyl ether, and completely miscible with all halogenated hydrocarbons and most of the common solvents. It is a powerful solvent for fats, fixed, mineral and essential oils, waxes, alkaloids, resins, tars, and is a latent solvent for cellulose derivatives. When used with a lower alcohol or ester, ethyl alcohol, or ethyl acetate, the mixture becomes a solvent for a large number of cellulose esters and ethers.

The anesthetic and toxic properties of chloroform bar its wider use as an industrial solvent. It is used medicinally in rubbing liniments and salves, as an anesthetic, as a preservative for serums, and as a vermicide. Some of its industrial uses are in plastics fabrication and film manufacture, as a



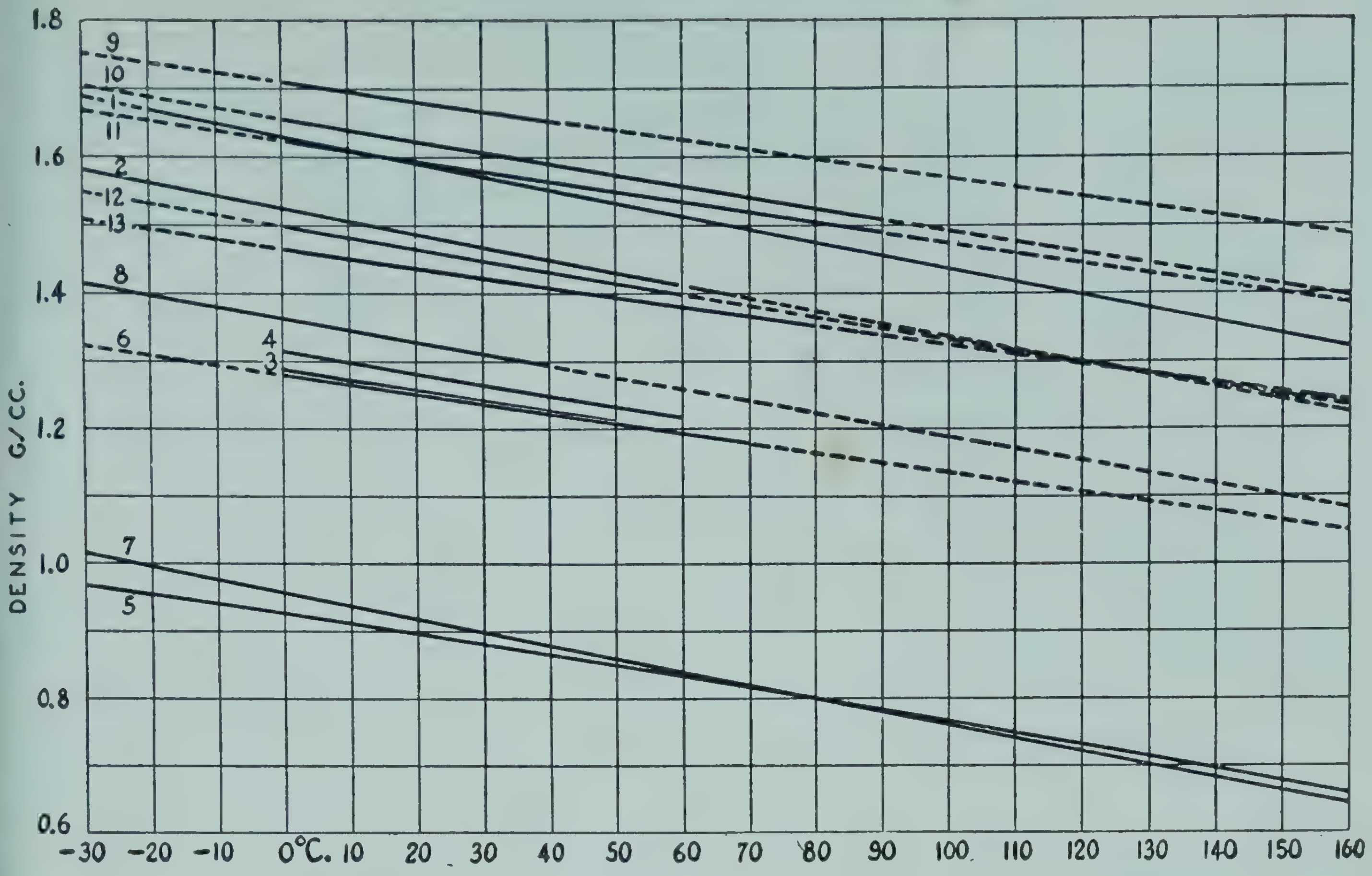
Solubility of Water in Chlorohydrocarbons



Viscosity of Liquids

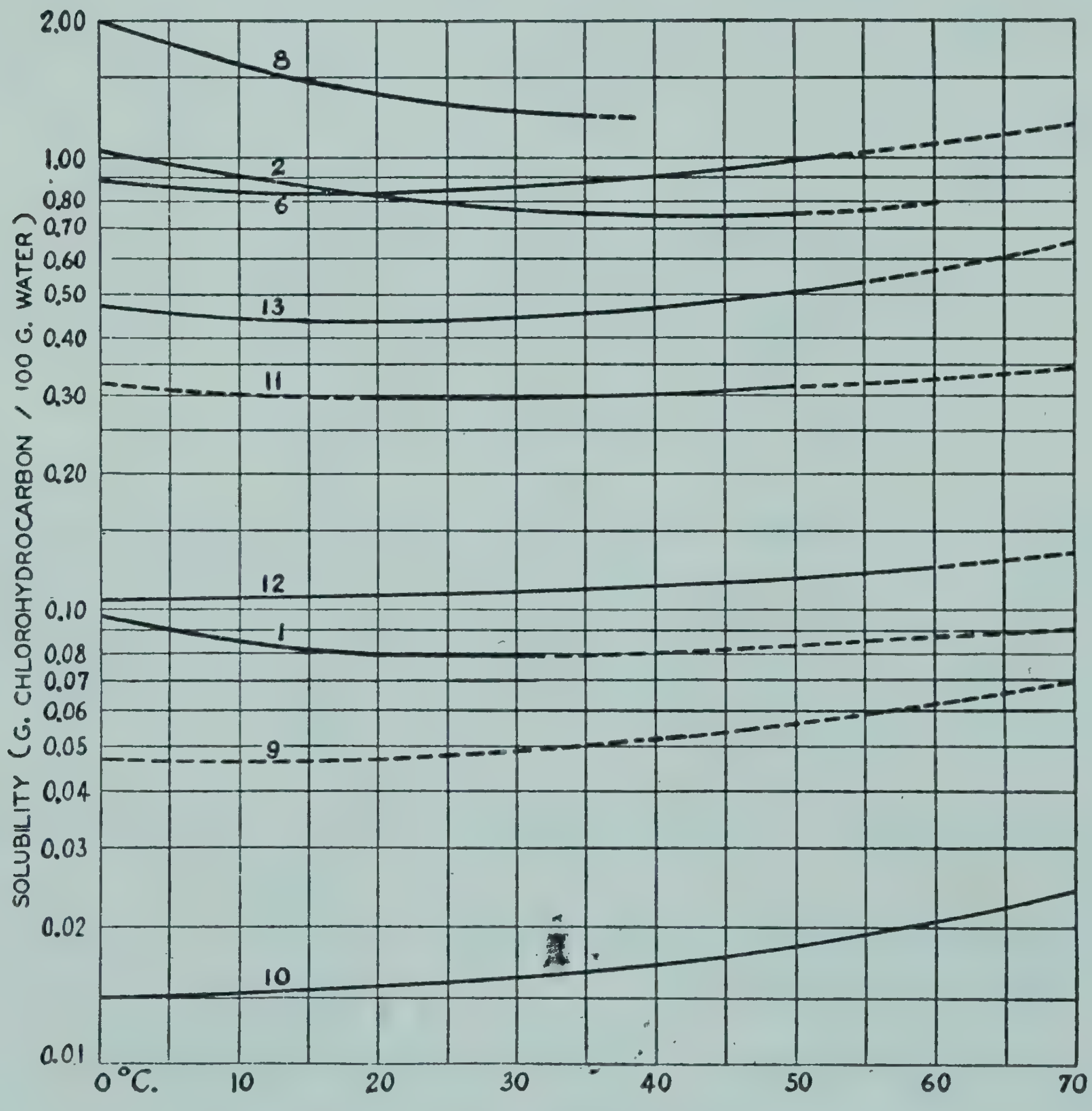
Figure 8.2. Properties of Halogenated Hydrocarbons.[6]

1. Carbon tetrachloride	3. *trans*-Dichlorethylene
2. Chloroform	4. *cis*-Dichlorethylene



Vapors in Air

(c)



(d)

Solubility of Chlorohydrocarbons in Water

5. Ethyl chloride	10. Perchlorethylene
6. Ethylene dichloride	11. Tetrachlorethane
7. Methyl chloride	12. Trichlorethylene
8. Methylene chloride	13. β-Trichlorethane
9. Pentachlorethane	

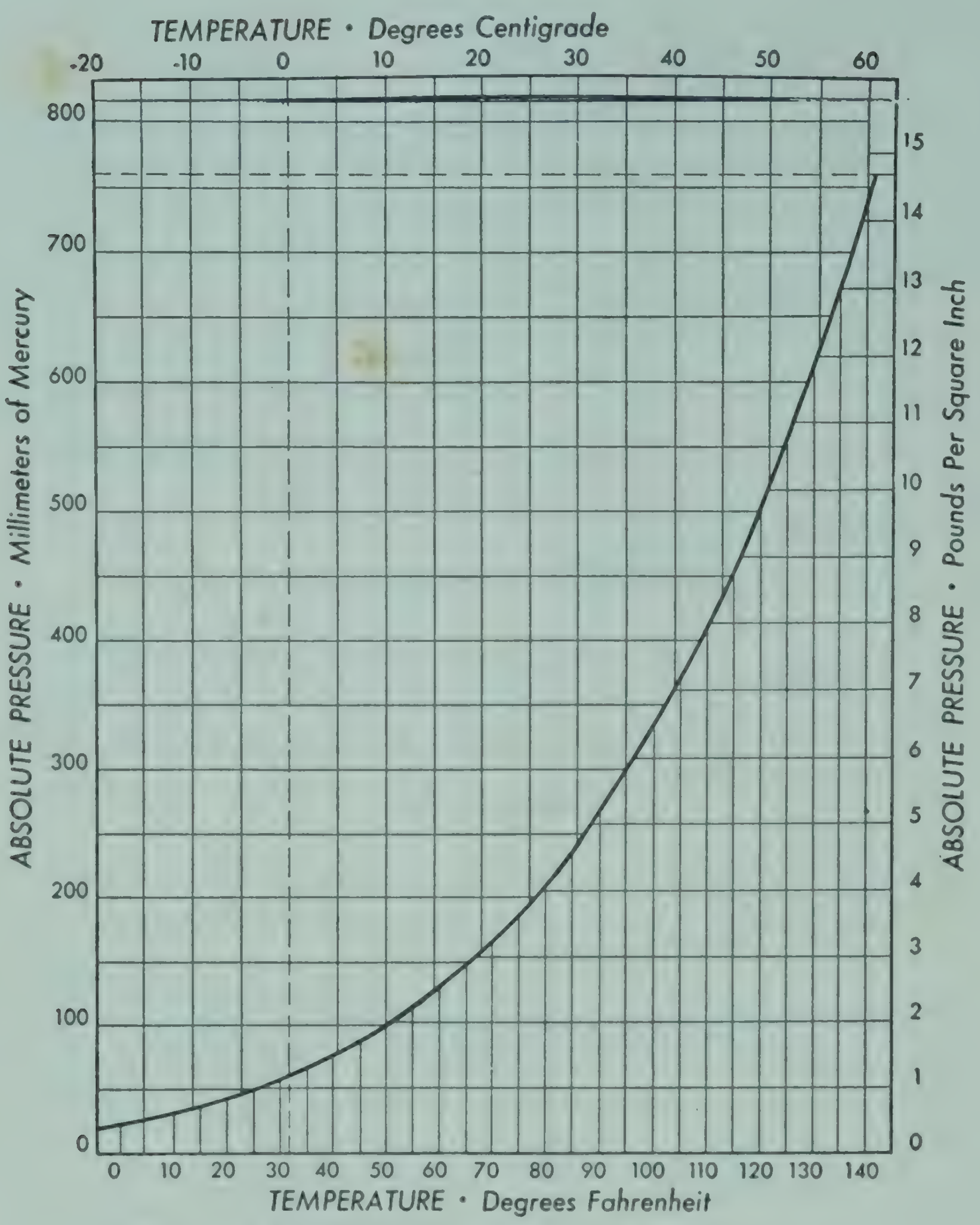


Figure 8.3. Vapor Pressures of Chloroform.[6]

cleaning and spotting agent for all textile fabrics other than those made from cellulose acetate, and as an extractant for oils, waxes, resins, rubber, sterols, etc. It is also in large demand for alkaloid assay in analytical work. Palmer and Kilbourne have made an extensive study of the reclamation of rubber by means of chloroform.[3]

Typical Properties and Specifications of Chloroform (Technical Grade)

Boiling point	61.2°C
Coefficient of cubical expansion Av./°C liquid	0.001399
Dielectric constant, 1000 cycle	4.90
Fire point	Nonflammable
Flash point	Nonflammable
Freezing point	63°C
Heat of evaporation at B.P.	59.0 cal./g.
Latent heat of evaporation at B.P.	59.1 cal./g. 106.4 B.t.u./lb.
Specific gravity at 25/25°C	1.477
Specific heat liquid at 20°C	0.234 cal./g./°C
Specific resistivity	4.0 × 10^9 ohms/cm.

Refractive index at *N* 20	1.4467
at 25°C	1.4422
Solubility in water at 20°C	0.82
Solubility of water in solvent at 10°C	0.06 gm./Water/100 gm.
Thermal conductivity, liquid	0.080 B.t.u./hr.(sq.ft.) (°F./ft.)
Vapor pressure at 30°C	243 mm
Vapor density (at B.P. and 760 mm)	4.36 g./liter
Viscosity at 20°C	5.63 millipoises
at 30°C	5.10 ”
Water (chart): no cloud at −10°C	0.021% by wt. maximum
Weight per gallon at 25°C	12.29 lbs.
Acidity (as HCl)	0.001% by wt. maximum
Boiling range at 760 mm	60.0 to 61.5°C
Color (max.)	Saybolt 24
Odor after evaporation	None

Carbon Tetrachloride (Tetrachloromethane) (CCl_4). Carbon tetrachloride is a heavy, colorless, nonflammable, and nonexplosive liquid of characteristic odor. It is miscible with acetic anhydride, ethyl alcohol, ethyl ether, naphtha, benzene, halogenated hydrocarbons, and with most solvents. It will dissolve fixed, mineral and essential oils, fats, greases, waxes,

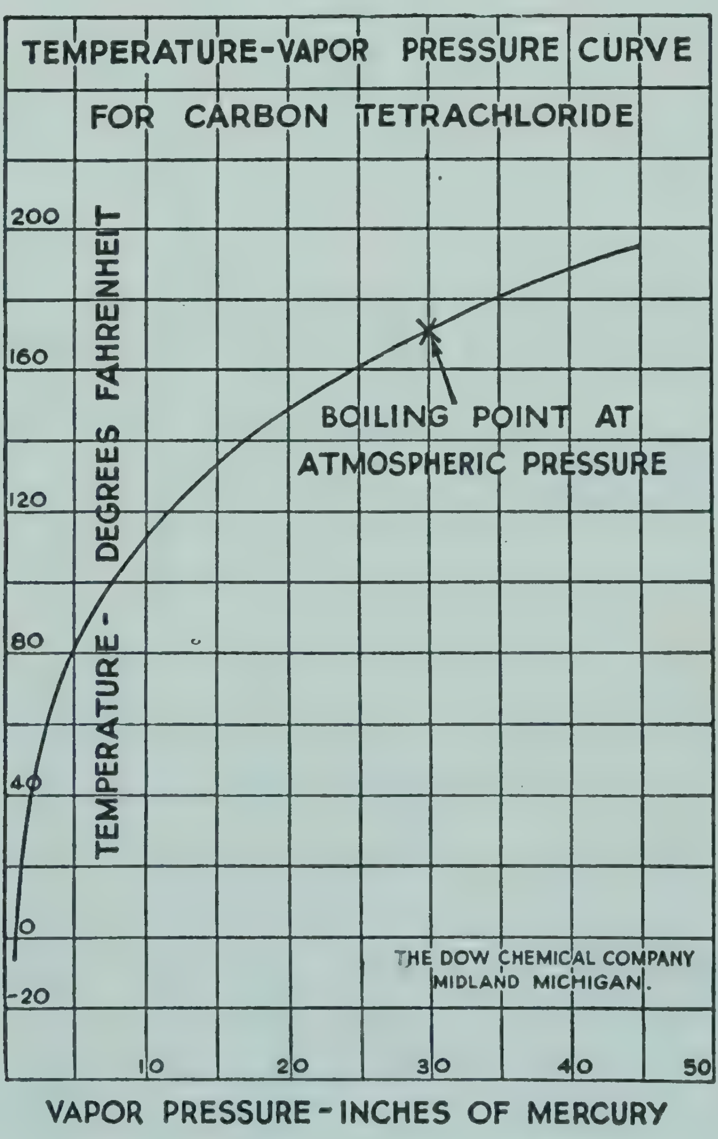


Figure 8.4. Temperature-Vapor Pressure Curve for Carbon Tetrachloride.[6]

TABLE 8.2. VAPOR PRESSURE OF CARBON TETRACHLORIDE[4]

TEMPERATURE		VAPOR PRESSURE MM. Hg
(°C.)	(°F.)	
0	32	33.4
10	50	56.3
20	68	91.3
30	86	141.1
33	91.4	158
44.3	111.8	250
62.3	144.2	480
76.55	169.8	764.5

TABLE 8.3. SOLUBILITY OF WATER IN CARBON TETRACHLORIDE[4]

TEMPERATURE		WATER IN SOLUTION GRAM PER 100 GRAMS OF CCl_4
(°C.)	(°F.)	
10	50	0.0071
20	68	0.0084
30	86	0.0109
40	104	0.0152
50	122	0.0237

TABLE 8.4. FLASH POINTS OF CARBON TETRACHLORIDE MIXTURES[4]

	% SOLVENT	% CCl_4	FLASH-POINT (°F)
Gasoline (Sp. Gr. 0.734 at 60°F)	50	50	Below 20
	40	60	" 20
	30	70	40
V. M. & P. naphtha (Sp. Gr. 0.746 at 60°F)	70	30	75
	60	40	100
	50	50	Above 170
	40	60	" 170
	30	70	" 170
Dry cleaners' naphtha (Sp. Gr. 0.745 at 60°F)	70	30	65
	60	40	90
	50	50	Above 170
	40	60	" 170
	30	70	" 170

TABLE 8.5. DECOMPOSITION OF CARBON TETRACHLORIDE[4]*

CARBON TETRACHLORIDE	BOILING POINT	20°C ABOVE B.P.	40°C ABOVE B.P.	60°C ABOVE B.P.
Dry				
In atmosphere of N_2	0	0	0	0
In oxygen	0.2	0	0	0
Saturated with water				
In atmosphere of N_2	0	0	0	0
In air and with soft steel	0	0.2	0.3	6.9
Excess of water				
In atmosphere of N_2	0.5	13.2	61	1066
In air and in presence of soft steel (refluxed)	172			

* Figures represent acidity in cc. of 0.01*N* HCl developed by 25 cc. C.T. in 24 hours.

TABLE 8.6. CORROSIVE ACTION OF CARBON TETRACHLORIDE ON SOFT STEEL[4]*

CARBON TETRACHLORIDE	BOILING POINT	20°C ABOVE B.P.	40°C ABOVE B.P.	60°C ABOVE B.P.
Saturated with water				
In atmosphere of N_2, with soft steel	0	0.1	0.2	0.6
In air, with soft steel	0.6	0.7	0.6	0.7
Excess of water				
In N_2, with soft steel (refluxed)	48.5			
In air, with soft steel	52.7	89.5	167	136

* Figures show loss of wt. of metal as mg./sq. in./24 hrs.

TABLE 8.7. CORROSIVE ACTION OF CARBON TETRACHLORIDE ON OTHER METALS[4]*

CARBON TETRACHLORIDE	BOILING POINT	20°C ABOVE B.P.	40°C ABOVE B.P.	60°C ABOVE B.P.
Saturated with water				
In air, with aluminum	0.7	0.9	381	358
In air, with tin	0.9	1.2	1.1	1.0
In air, with copper	0.9	1.2	1.1	1.0

* Figures show loss of wt. of metal as mg./sq. in./24 hrs.

TABLE 8.8. EVAPORATION OF A CARBON TETRACHLORIDE-NAPHTHA MIXTURE[4]

% OF SAMPLE EVAPORATED	COMPOSITION OF RESIDUE BY VOL.		FLASH-POINT OF RESIDUE	% OF CONSTITUENTS OF ORIGINAL MIXT. EVAPORATED	
	% CCl_4	% Naphtha		CCl_4	Naphtha
0	43	57	No flash up to incipient boiling.		
37	29	71	104°F	57.6	21.7
70	5	95	86°F	96.5	50.0
87	1	99	90°F	99.7	77.2

TABLE 8.9. EVAPORATION RATE OF CARBON TETRACHLORIDE MIXTURES[4]

SOLVENT	RATE OF FREE EVAPORATION AT ROOM TEMP.	
	(cc. per hour per 100 $cm.^2$)	(Gallon per 24 hrs. per square foot)
Carbon tetrachloride	4.30	0.254
C.T.-Naphtha cleaning fluid		
0–37% evaporated	2.77	0.163
37–70% "	2.06	0.123
70–87% "	0.80	0.047
Weighted average 87% evaporated	2.12	0.125

TABLE 8.10. SOLUBILITY OF SOME GUMS AND RESINS[7]

SUBSTANCE	ETHYLENE DICHLORIDE	80% ETHYLENE DICHLORIDE 20% DENATURED ALCOHOL	SUBSTANCE	ETHYLENE DICHLORIDE	80% ETHYLENE DICHLORIDE 20% DENATURED ALCOHOL
Amberol	S	S	Kauri	I	S
Albertol	S	S	Manila	S	S
"Bakelite"	S	S	Manila ester	S	S
Coumarone	S	S	Mastic	SS	S
Camphor	S	S	Rosin	S	S
Dammar	S	PS	Glyptol	S	S
Elemi	SS	S	Sarpee	I	S
Ester gum	S	S	Sandarac	SS	S
Guaiac	SS	S	Shellac	SS	S
Gilsonite	S	S	"Vinylite A"	S	S
			"Vinylite 80"	S	I

S = soluble. SS = slightly soluble. PS = partially soluble. I = insoluble.

TABLE 8.11. SOLUBILITY OF VARIOUS DYES IN CARBON TETRACHLORIDE[5]

DYE	MIN. CC. TO DISSOLVE 0.5 GRAM DYE	DYE	MIN. CC. TO DISSOLVE 0.5 GRAM DYE
Sudan I	5	Sudan III	20
Maroon I	5	Azo turkey red	20
Sudan VIII	5	Cloth red G	20
Chrome fast yellow	5	Sudan G	25
Rose	5	Maroon II	25
Sudan VII	5	Cloth red BB	25
Scarlet H	5	Fast brown O	25
Walnut	5	Maroon III	25
Sudan II	5	Sudan brown	25
Xylidine brown	5	Chrysamine G	25
Indiana red	5	*p*-Nitroaniline red	35
Oil maroon	5	Alizarin yellow R	35
Azo coccine RR	8	Aniline yellow G	35
Xylidine red N	8	Cardinal	35
Xylidine brown M	10	Benzidine puce	35
Sudan IX	10	Benzidine puce A	35
Sudan X	10	Indoine blue	35
Naphthol black	10	Congo red A	60
Oil Scarlet	10	*m*-Nitroaniline orange	60
Sudan R	15	Alizarin yellow GG	60
Fast Red A	15	Benzidine brown	100 Inc.
Oil brown	15	Diazine green	100 Inc.
Spirit yellow	20	Diazine black	100 Inc.

gums, camphor, metallic resinates, bitumens, asphalt, unvulcanized rubber, some cellulose ethers, and such resins as "Bakelite," coumarone, dammar, ester gum, elemi, guaiac, mastic, sandarac, rosin, and alkyd and vinyl resins. In the presence of a lower aliphatic alcohol or acetate, the solvent power of carbon tetrachloride for cellulose esters and ethers is increased. When decomposed it may produce poisonous gases, such as phosgene, chlorine, and hydrochloric acid.

Carbon tetrachloride is used extensively as a solvent and diluent, and in the extraction of oils from their seeds, grease from bones and hides, and alkaloids from plants. It is a solvent for bitumens, asphalt, gums, antimony trichloride, cholesterol, and is used in rubber cements. It is also a solvent in floor waxes and furniture polish, and in paints and varnishes. Carbon tetrachloride finds wide application in fire extinguishers for home and industry as indicated in the following table of allocations. It is also used in grain fumigation, moth control, as a delousing agent, as a diluent in chlorination, and as a constituent part in dry cleaners' soap. It is a starting point in the synthesis of many organic chemicals, dyes and drugs. It lowers the flammability hazard of organic solvents, as mentioned previously (see Table 8.4).

Allocations of Carbon Tetrachloride: July 1, 1944–June 30, 1945
(Thousands of pounds pure)

	TOTAL		JAN. 1–JUNE 30, 1945	JULY 1–DEC. 31, 1944
	Amount	Per cent		
Total Allocations	223,092	100.0	112,330	110,762
Direct military[1]	56,885	25.5	33,019	23,866
Foreign	2,422	1.1	1,140	1,282
Other uses	163,785	73.4	78,171	85,614
Fire extinguishers	94,291	42.3	47,299	46,992
Degreasing compounds	31,511	14.1	8,503	23,008
Dry cleaning	10,892	4.9	6,450	4,442
Agriculture	4,837	2.1	2,506	2,331
Drugs	3,549	1.6	1,685	1,864
Synthetic rubber	3,366	1.5	1,737	1,629
Miscellaneous uses and small orders	15,339	6.9	9,991	5,348

[1] End-use data not available.

Typical Properties and Specifications

Boiling point (760 mm)	76.7°C (170.1°F)
Coefficient of cubical expansion Av./°C Liquid	0.00127
Dielectric constant, 1000 cycle	2.24
Electrical conductivity	4 × 10^{-18} recip. ohm
Fire point	Nonflammable
Flash point	Nonflammable
Freezing point	−23°C
Heat of fusion	4.2 cal./kg.
Heat of vaporization	46.5 cal./g.
Power factor, 1000 cycle	0.057%
Purity	99.99%, min.
Residue	0.0010% by wt., maximum
Specific gravity at 25°/4°C	1.5845
Specific heat, cal./gm./°C, Liquid at 25°C	0.1995
at 76.8°C	0.2157
Specific resistivity	3.8 × 10^{12} ohms/cm.
Refractive index at 20°C	1.4607
Solubility in water at 20°C	0.08% by wt.
Solubility of water in solvent at 20°C	0.008% by wt.
Thermal expansion per °C	0.127% (of liquid at 158°F)
Vapor density (at B.P. and 760 mm)	5.37 g./liter
Vapor pressure at 30°C	140 mm
Viscosity liquid at 20°C	0.96 centipoises
Weight per gallon at 25°C	13.22 lbs.
Acidity as HCl	None
Boiling range	Within 1°C
Odor residual	None

Ethyl Chloride (Monochloroethane, muriatic ether) (C_2H_5Cl). Ethyl chloride is a colorless, volatile and flammable liquid having an ether-like odor. In the absence of water it is stable and noncorrosive but it hydrolyzes in the presence of water or alkalies. It is miscible with ethyl ether, carbon tetrachloride and most of the commonly used solvents; but it is partially soluble in ethyl alcohol and only slightly soluble in water. It is a solvent for phosphorus, fats, oils, resins, waxes, etc. It is used as a solvent, a local anesthetic, insecticide, refrigerant, in the preparation of dyes and drugs, and as an ethylating agent. Addition of a lower aliphatic alcohol or acetate, greatly improves the solvent power of ethyl chloride and other chlorinated ethanes, such as the dichloro-, trichloro-, tetrachloro-, and pentachloroethanes.

Typical Properties and Specifications

Boiling point	12.3°C
Coefficient of expansion Av./°C liquid	0.0021
Critical point	187°C and 52 atm.
Dielectric constant of liquid at 170°C	6.29
Flash point	Below 32°F
Freezing point	−139°C
Heat of combustion (gas)	316.7 kg. cal./mol.
Latent heat of evaporation at B.P.	92.5 cal./g. or 165.6 B.T.u./lb.
Specific gravity at 0/4°C	0.923
Specific heat at 0°C	0.37 cal./g. or B.T.u./lb.
Refractive index at 0°C	1.1179
Solubility in water at 20°C	0.574 g. per 100 g. solvent
Solubility of water in solvent at 21°C	48.3 g. per 100 g. solvent
Vapor density at B.P. and 760 mm	2.76 g./liter
Vapor pressure at −30°C	107.4 mm
−20	180.3
−10	289.1
0	450
10	678
20	1000
Viscosity liquid at 20°C	0.1 centipoise
Water content, no cloud at −15°C	0.011% by wt., max.
Weight per gallon at 0°C	7.70 lbs.
Acidity as HCl	0.0002% by wt., max.
Boiling range at 760 mm	12.2 to 12.6°C
Color	Water-white
Non-volatile matter	0.001% by wt., max.
Purity	Contains less than 0.04% acid and less than 0.05% Alcohol

Ethylene Dibromide (1,2-Dibromoethane, ethylene bromide) (CH_2Br-CH_2Br). Ethylene dibromide is a heavy, colorless, nonflammable, stable liquid having a sweet odor. It is insoluble in water but soluble in ethyl ether, ethyl alcohol, carbon tetrachloride and in most solvents and thin-

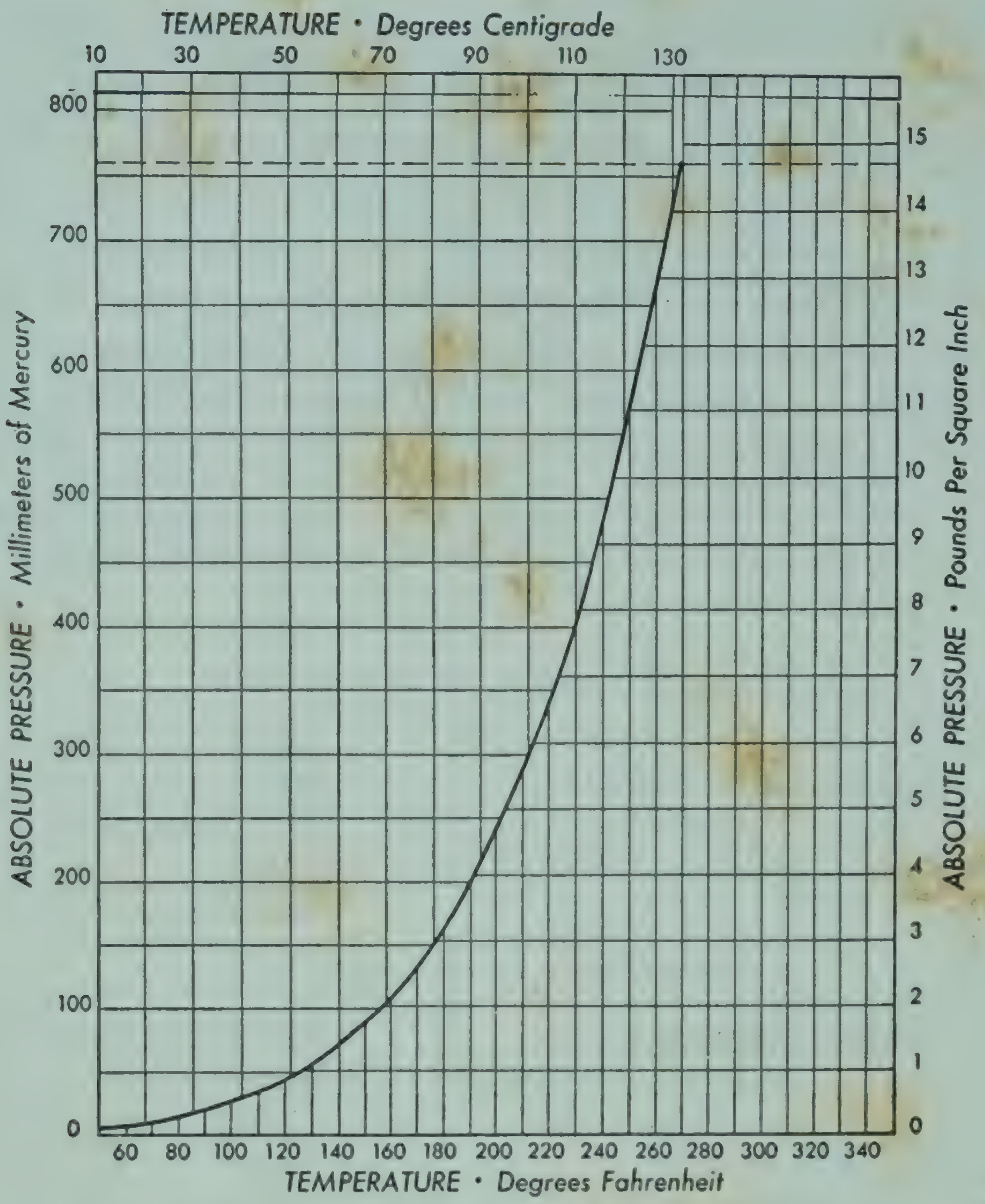


Figure 8.5. Vapor Pressures of Ethylene Dibromide.[6]

ners, and it will dissolve oils, fats, gums, waxes, resins, "Celluloid," etc. It is principally used as a solvent in tetraethyl lead anti-knock solutions (Ethyl Fluid). Since it exerts a powerful dissolvent action upon gums, it is used as a constituent part of lubricating gasolines. It is also used in the synthesis of drugs and dyes. In medicine it is used as an anaesthetic, antispasmodic and sedative.

Typical Properties and Specifications

Boiling point	131.4°C
Density at 10°C	2.2014
20	2.1805
30	2.1594
40	2.1384
60	2.0952
80	2.0538
100	2.0113
Dielectric constant, 1000 cycle	5.17
Fire point	Nonflammable

Flash point	Nonflammable
Freezing point	9.3°C
Latent heat of fusion at 9.55°C	56.62 joules/g.
Latent heat of vaporization at 130.8°C	193.5 joules
Specific gravity at 25/25°C	2.172
Specific heat	0.18 cal./g./°C
Specific resistivity	2.4 × 10^9 ohms/cm.
Refractive index at 25°C	1.5357
Surface tension at 20°C	38.71 dynes/cm.
Vapor pressure at −10°C	2.5 mm
0	3.9
10	6.03
30	17.4
50	44.3
70	101.0
100	295
120	552
131	760
Weight per gallon at 25°C	18.07 lbs.
Acidity (0.01*N* NaOH/100 cc)	less than 1 cc.
Boiling range	90% within 2.0°C

Ethylene Chlorobromide (2-Bromo-1-chloroethane, *sym.*-chlorobromoethane) (CH_2ClCH_2Br). Ethylene chlorobromide is a colorless, volatile liquid with a chloroform-like odor. It is insoluble in water but miscible with ethyl alcohol, ethyl ether, carbon tetrachloride and most organic solvents. It possesses the distinctive property of dissolving both cellulose esters and ethers. It is used as a solvent and in organic synthesis.

Boiling point	106.1°C
Fire point	Nonflammable
Flash point	Nonflammable
Freezing point	−18.4°C
Specific gravity at 25/25°C	1.720
Solubility in water at 30°C	0.69 g. per 100 g. solvent
at 80°C	0.7
Weight per gallon at 25°C	14.31 lbs.
Boiling range	5–95%, not more than 2.0°C

Ethylene Dichloride (1,2-Dichloroethane, *sym.*-dichloroethane, ethylene chloride, Dutch oil, elayl chloride) ($ClCh_2$—CH_2Cl). The synonym "Dutch oil" owes its origin to the four Dutch chemists who in 1795 were first to prepare this compound. It is a colorless, stable, mobile and volatile liquid resembling chloroform in its odor and toxicity. It is manufactured by the chlorination of ethane or ethylene. It is insoluble in water but soluble in ethyl alcohol, ethyl ether, carbon tetrachloride and miscible in all proportions with most common solvents. Ethylene dichloride is a good solvent for oils, fats, waxes, some alkaloids, unvulcanized rubber, camphor, benzyl

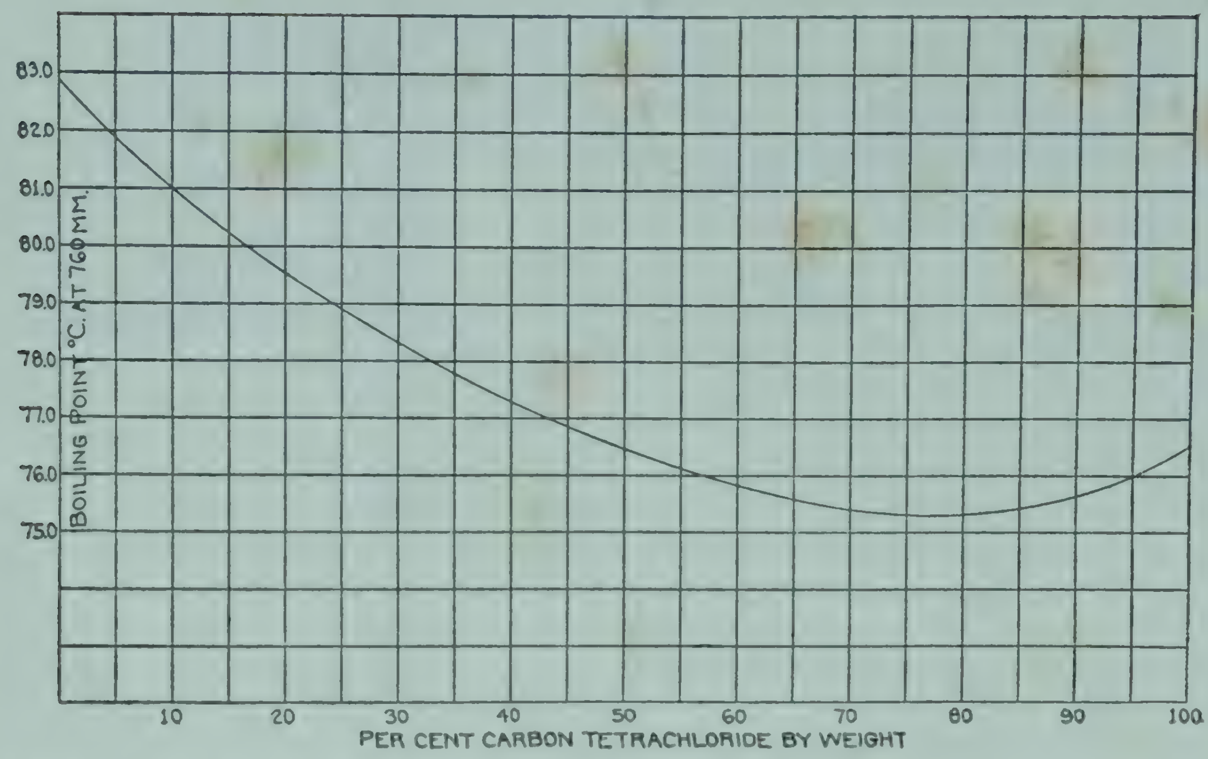


Figure 8.6. Boiling Point of Ethylene Dichloride-Carbon Tetrachloride Mixtures at 760 mm.

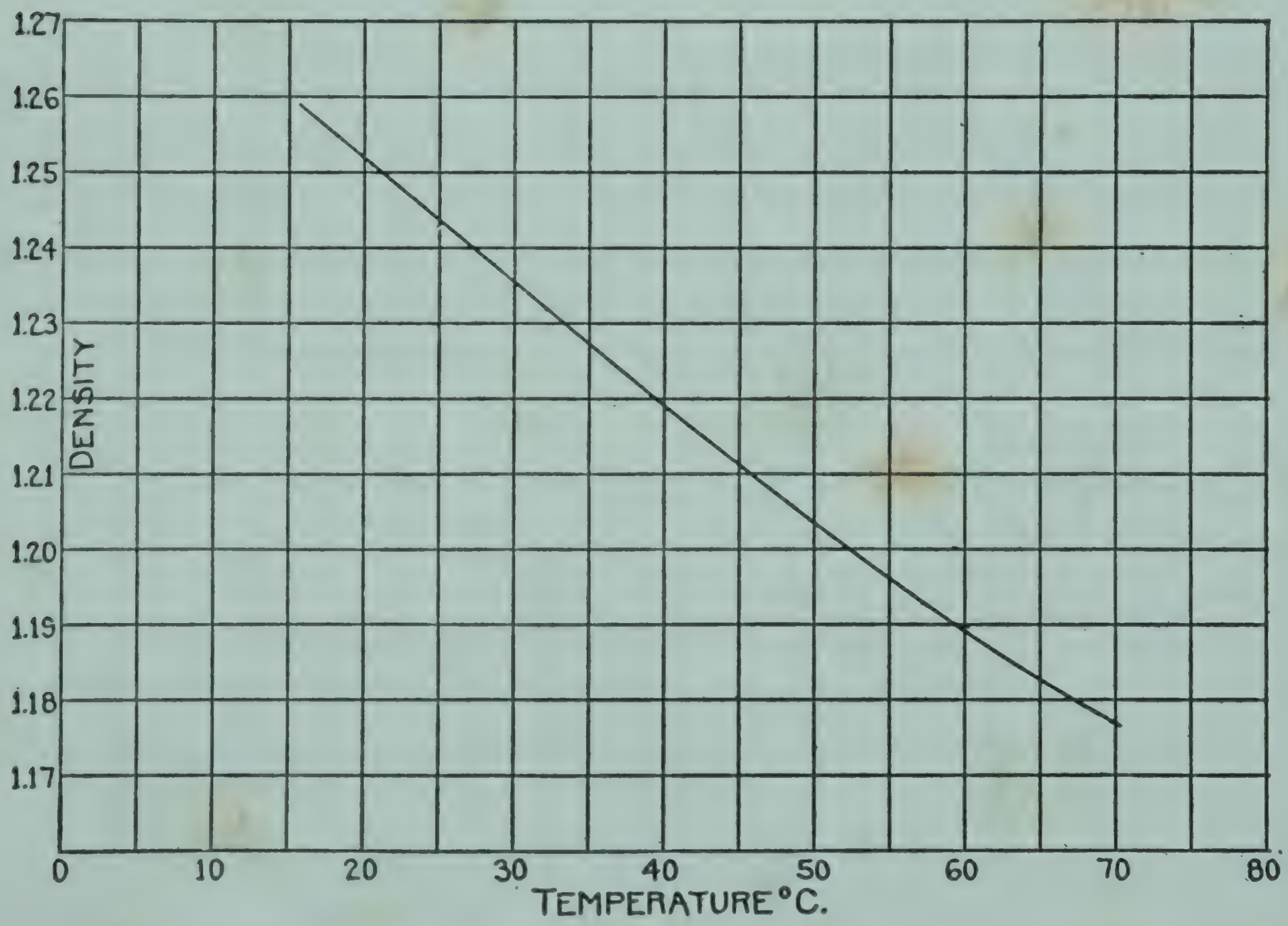


Figure 8.7. Density of Ethylene Dichloride at Various Temperatures.[7]

abietate, coumarone resins, dammar, guaiac resin, mastic, rosin, sandarac, phenolic, acrylic and vinyl resins, metallic resinates, gums, and so forth, and it will dissolve some cellulose ethers. Its solvent power is greatly improved for a large number of cellulose ethers and esters when mixed with ethyl or methyl alcohol, or ethyl or methyl acetate.

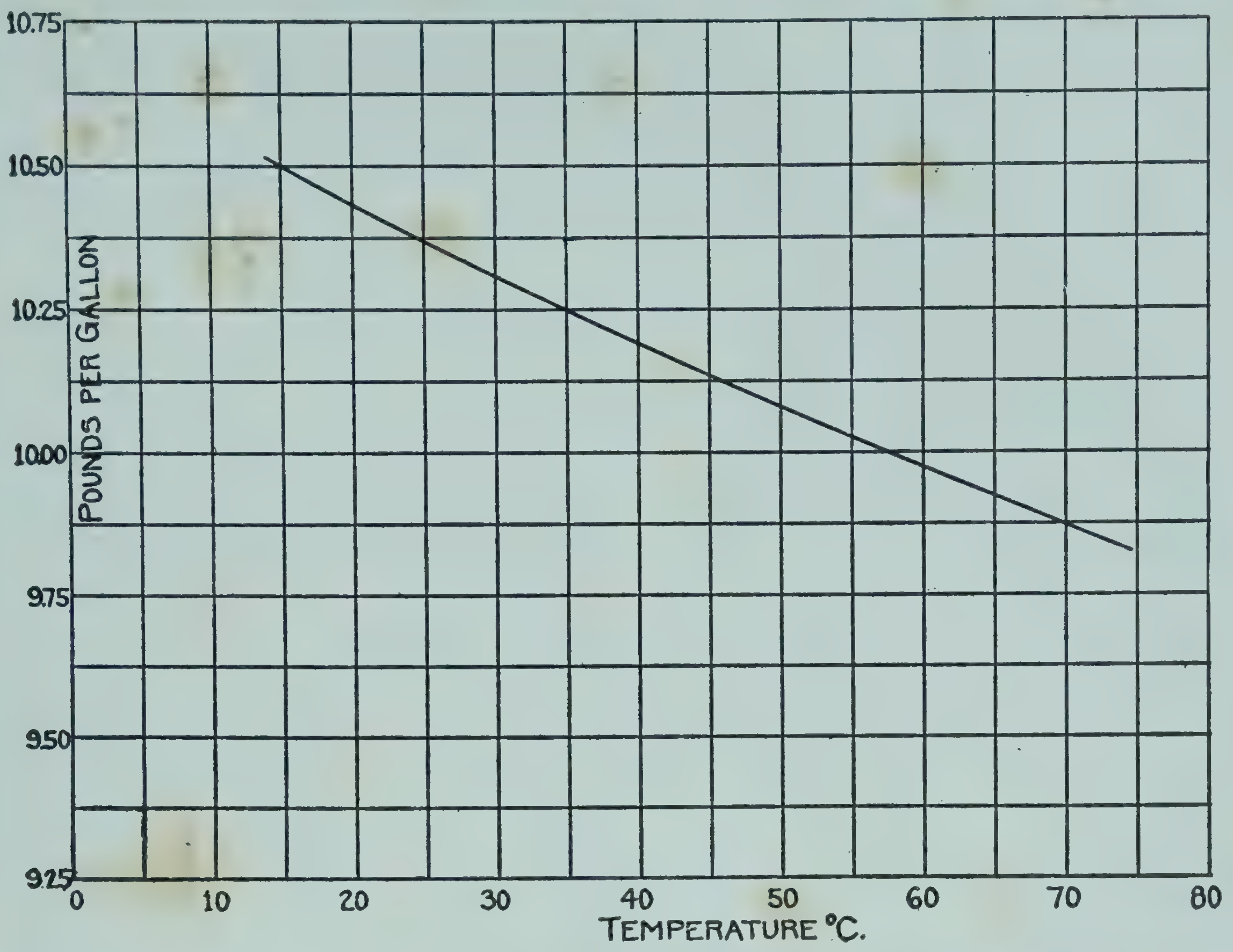


Figure 8.8. Weight per Gallon of Ethylene Dichloride at Various Temperatures.[7]

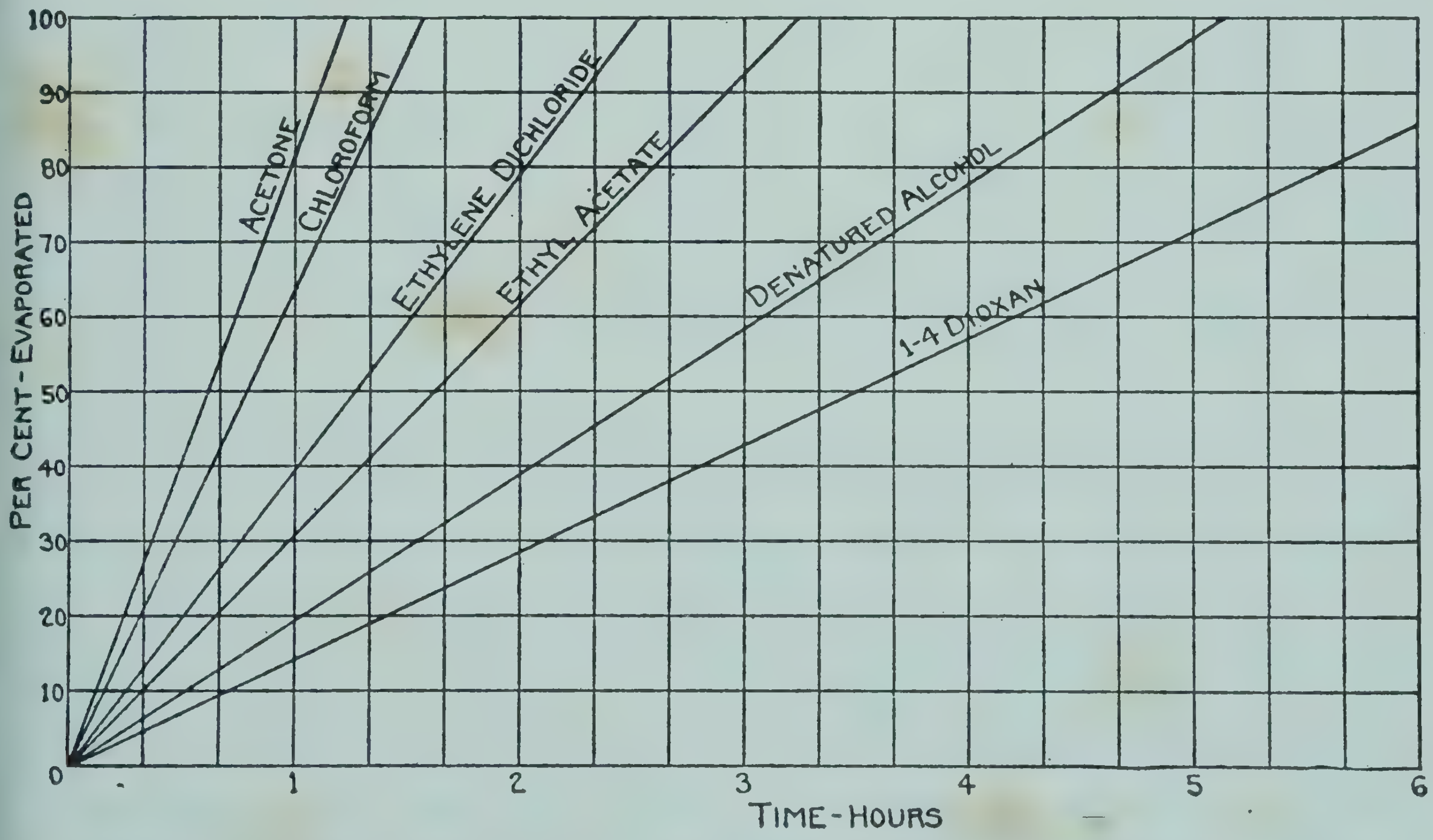


Figure 8.9. Evaporation Rate of Various Solvents at Room Temperature[7]

Since ethylene dichloride shows satisfactory stability toward hydrolysis under normal conditions of usage its desirability as a solvent is receiving wider attention. It is also resistant to oxidation, does not corrode metals, and burns with difficulty, though it supports combustion.

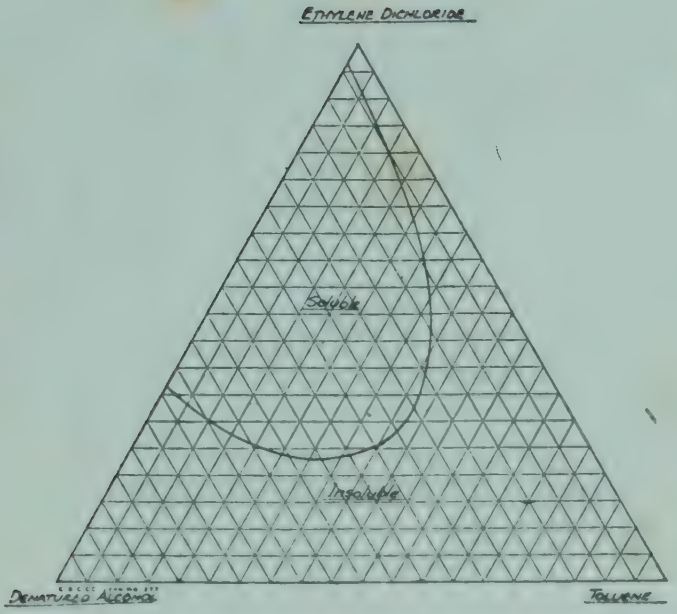


Figure 8.10.
Solubility of Cellulose Acetate in Mixtures of Ethylene Dichloride, Denatured Alcohol, and Toluene.[7]

TABLE 8.12. DILUTION RATIOS[7]

SOLVENT	ETHYLENE DICHLORIDE	TOLUENE	V. M. & P. NAPHTHA
Acetone	8.6	4.6	0.73
Solvatone[a]	6.8	4.0	0.68
Ethyl acetate	5.4	3.5	1.20
Isopropyl acetate	4.3	3.1	1.25
Methyl "Cellosolve"	9.2	4.3	0.35
Butyl acetate	3.7	2.5	1.35
"Cellosolve"	7.6	4.7	0.95
Butyl propionate	2.7	2.5	1.20
"Cellosolve" acetate	4.2	2.5	0.80
Pentacetate	3.5	1.9	1.27
Butyl "Cellosolve"	4.3	3.0	1.85

[a] Solvatone is a mixture consisting of approximately 80 per cent acetone, 10 per cent isopropyl alcohol and 10 per cent toluene.

This cheap and readily available solvent is extensively used in the extraction of edible oils from oil-bearing seeds, vitamins from fish-liver oils, and residual oil from oil cakes. A mixture composed of three parts ethylene dichloride and one part carbon tetrachloride is used as a nonexplosive, noninjurious fumigant for furniture, furs, cereals, grains, flour, dried fruit and nuts. It is a component of lead tetraethyl anti-knock fluid and is used in the extraction of pyrethrum flowers. Ethylene dichloride is employed in the textile industry for degreasing wool, as a spotting agent for the removal of tar, paint, and brand marks, in soap scouring compounds, and in wetting out, penetrating, and degumming compounds. In combination with carbon tetrachloride it is used in dry-cleaning and spotting fluids. It is used as a lacquer solvent, in paint, varnish and finish removers, in degreasing metals, and in chemical synthesis. It is also an extractive agent of nicotine from tobacco.

TABLE 8.13. ETHYLENE DICHLORIDE IN COMBINATION WITH VARIOUS SOLVENTS[7]

FORMULAE	1	2	3	4	5	6	7	8	9	10
Cellulose-acetate lacquers										
Ethylene dichloride	70	70	70	60	50	50	70	70	40	60
Toluene									20	
Denatured alcohol	20	20	20	10	10	15			10	15
Ethyl acetate				15						
"Solvatone"							15			
Methyl "Cellosolve"	10			10	30	20	15	20	30	10
1,4-Dioxan						15		10		
Diacetone alcohol					10					
"Cellosolve" acetate				5						15
Ethyl lactate		10								
Butyl "Cellosolve"			10							
Base-lacquer solvents										
Ethylene dichloride	40	50	75	30	30	70	35	25		
Toluene	30	20		30	30		30	40		
Denatured alcohol	10	10	15				10	5		
Butyl alcohol				15	10	10	5			
Ethyl acetate	10			10	10			15		
Butyl acetate		10	10		15		15			
"Cellosolve"	5	5		10		10		10		
Pentacetate					5					
"Cellosolve" acetate	5			5		10				
Butyl "Cellosolve"		5					5	5		
Thinners										
Ethylene dichloride	72	67	45	40	40	35	40			
Toluene			30	30	35		30			
Xylene						30				
Denatured alcohol	25		10	10	13	15	15			
Butyl alcohol		25								
Ethyl acetate	3			10	7	10	5			
"Cellosolve"				7	3		5			
"Cellosolve" acetate		8			2	10				
Butyl acetate			10							
Pentacetate			5							
Butyl "Cellosolve"				3			5			

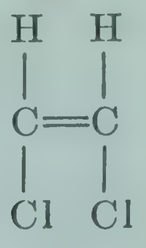
Typical Properties and Specifications

Apparent ignition temperature in air	449°C
Boiling point	83.6°C
Coefficient of cubical expansion Av./°C liquid 10°–30°C	0.00116
Dielectric constant at 20°C	10.5 ± 0.3
Electrical conductivity	3×10^{-8}
Explosive limits in air	6.2–15.9% by vol.
Fire point	28°C
Flash point (A.S.T.M. Open Cup)	21°C
Freezing point	−35°C
Heat of combustion	2720 cal./g.
Latent heat of evaporation at B.P.	77.3 cal./g.
Specific gravity at 20/20°C	1.2550
Specific heat	0.31 cal./g./°C
Specific resistivity	9.0×10^{6} ohms/cm.
Refractive index	1.4443
Surface tension at 25°C	37.5 dynes/cm.
Solubility in water at 20°C	0.87% by wt.
Solubility of water in solvent at 20°C	0.16% by wt.
Thermal conductivity at 20°C	0.0038 cal./cm./sec./°C
Vapor density (at B.P. and 760 mm.)	3.88 g./liter
Vapor pressure at 20°C	63 mm
30°C	99 mm
Viscosity at 25°C	0.0078 poise
Water content	Not more than 0.02%
Weight per gallon at 25°C	10.38 lbs.
Acidity, calculated as HCl	Not more than 0.001%
Boiling range (760 mm)	Below 82.5°C None Above 84.0°C None
Color (500-mm tube)	Not more than 1.0 yellow Lovibond
Non-volatile matter	Not more than 0.001 g./100 cc.
Purity	Not less than 99.0%

Azeotropic Mixtures

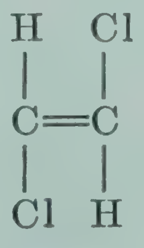
	% by Wt.			B.P. (°C)
Ethylene dichloride	78.6	Ethyl alcohol	21.4	70.5
Ethylene dichloride	86.8	Methyl alcohol	13.2	59.5
Ethylene dichloride	91.8	Water	8.2	70.5
Ethylene dichloride	78.0	Ethyl alcohol	17	66.7
		Water	5	

Dichloroethylene (*cis*-Acetylene dichloride, *trans*-acetylenedichloride)



$$\begin{matrix} H & & H \\ | & & | \\ C & = & C \\ | & & | \\ Cl & & Cl \end{matrix}$$

cis



$$\begin{matrix} H & & Cl \\ | & & | \\ C & = & C \\ | & & | \\ Cl & & H \end{matrix}$$

trans

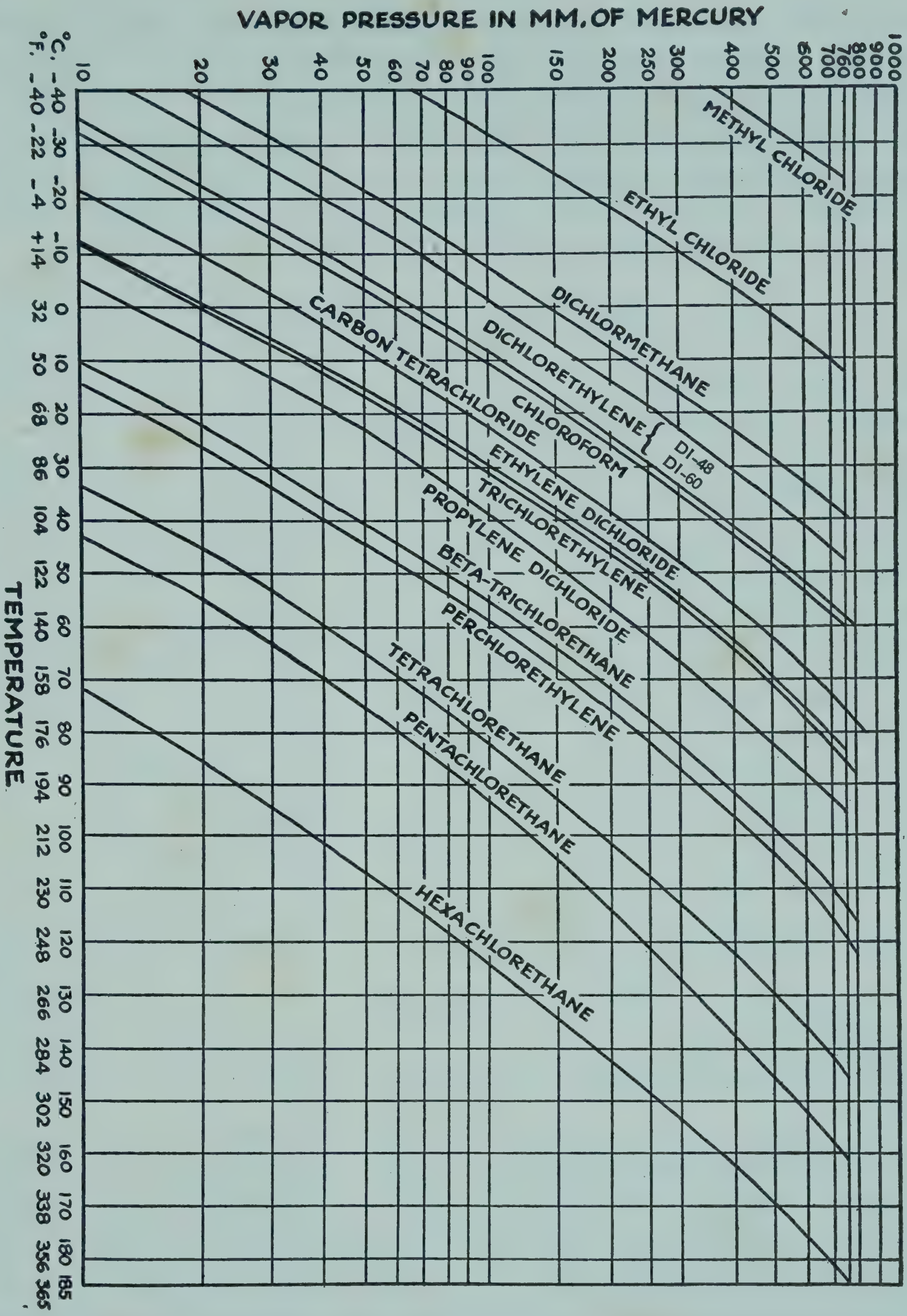


Figure 8.11. Vapor Pressure of Various Solvents at Different Temperatures.[7]

Dichloroethylene is a mixture of stereoisomeric compounds made by the partial chlorination of acetylene. Its physical properties are determined by the different isomers present in its composition. It is a colorless, low-boiling liquid with a pleasant odor. The hot vapors of this solvent can be ignited but will not continue to burn unless heat is supplied. However, there is little danger in its general use. It is insoluble in water but soluble in ethyl alcohol, ethyl ether, benzene, and carbon tetrachloride. It is a good solvent for oils, gums, resins, waxes, unvulcanized rubber, shellac, and cellulose acetate. When mixed with ethyl or methyl alcohol or alkyl acetates it shows a pronounced solvency for the ester and ether derivatives of cellulose. It is used in the extraction of dyes, perfumes and organic material, in lacquers, thermoplastics, and as a rubber solvent.

Typical Properties and Specifications

cis isomer

Boiling point (760 mm)	60.3°C
Coefficient of cubical expansion Av./°C liquid	0.00127
Flash point	6°C
Freezing point	−80.5°C
Latent heat of vaporization (at B.P.)	73.0 cal./g.
Specific gravity at 20/4°C	1.282
Specific heat at 20°C (liquid)	0.270 cal./g./°C
Refractive index at 15°C	1.4519
Solubility in water at 25°C	0.77 g./100 g.
Solubility of water in solvent at 10°C	0.04 g. water/100 g.
Vapor density (at B.P. and 760 mm)	3.54 g./liter
Vapor pressure at 30°C	273 mm
Viscosity (liquid at 20°C)	0.48 centipoises
Water: no cloud at −15°C	0.001% by wt., max.
Weight per gallon at 20°C	10.70 lbs.
Acidity (as HCl)	0.0005% by wt., max.
Boiling range (760 mm)	57.5 to 61.0°C
Color	Saybolt No. 24 max.
Residue on evaporation	0.007% by wt., max.

trans isomer

Boiling point (760 mm)	48.0 to 48.5°C
Coefficient of cubical expansion: Av./°C liquid	0.00136
Flash point	4°C
Freezing point	−50.0°C
Latent heat of vaporization (at B.P.)	73.7 cal./g.
Solubility in water at 25°C	0.63 g./100 g.
Solubility of water in solvent at 10°C	0.03 g. water/100 g.
Specific gravity at 20/4°C	1.257
Specific heat at 20°C (liquid)	0.270 cal./g./°C
Refractive index at 15°C	1.4490
Vapor density (at B.P. and 760 mm)	3.67 g./liter
Vapor pressure at 30°C	395 mm
Viscosity liquid at 20°C	0.41 centipoise
Water: no cloud at −15°C	0.004% by wt., max.
Weight per Gallon at 20°C	10.49 lbs.
Acidity (as HCl)	0.0005% by wt., max.
Boiling range (760 mm)	47.0 to 48.5°C
Color	Saybolt No. 24 max.
Residue on evaporation	0.0007% by wt., max.

Beta-Trichloroethane ($CH_2ClCHCl_2$). Beta-trichloroethane is a colorless, nonflammable liquid, miscible with alcohols, ethers, ketones, etc. Like most chlorinated solvents it will dissolve oils, fats, waxes, tar, many natural and synthetic resins and alkaloids. It will also dissolve cellulose acetate when mixed with alcohol. It is used principally as an intermediate for the manufacture of vinylidene chloride for plastics.

Boiling point (760 mm)	113.5°C
Fire point	Nonflammable
Flash point	Nonflammable
Freezing point	−36.7°C
Latent heat of evaporation (at B.P.)	68.7 cal./g.
Solubility in water at 25°C	0.48 g./100 g.
Solubility of water in solvent at 20°C	0.03 g. water/100 g.
Specific gravity at 20/4°C	1.441
Specific heat at 20°C (liquid)	0.266 cal./g./°C
Specific resistivity	5.2×10^8 ohms/cm
Refractive index	1.4711
Vapor density (at B.P. and 760 mm)	4.21 g./liter
Vapor pressure at 30°C	36 mm
Vapor pressures	

(°C)	(°F)	(mm Hg)
90	194	369
100	212	505
110	230	680
114	237	764

Water	0.007% by wt., max.
Weight per gallon at 20°C	12.04 lbs.
Acidity (as HCl)	0.0001% by wt., max.
Boiling range (760 mm)	111.8 to 113.3°C (5–95%)
Free halogen	None
Non-volatile matter	None

Trichloroethylene (1,2,2-Trichloroethylene, ethylene trichloride, "Westrosol", Tri) ($CHCl{=}CCl_2$). Trichloroethylene is a heavy, low-boiling colorless, mobile liquid with a pleasant, chloroform-like odor. It is quite stable, nonflammable, nonexplosive, and will not attack the common metals even in the presence of moisture. The first record of the preparation of trichloroethylene was in 1864 by the reduction of hexachloroethane with hydrogen. Germany started its commercial manufacture in 1910, but the United States is now producing it on an extensive scale.

It is insoluble in water but soluble in most organic solvents, some of which are acetone, ethyl ether, benzene, toluene, pyridine, amyl, butyl, ethyl and methyl acetates or alcohols and mixtures of these solvents. It dissolves cellulose ethers and some types of cellulose acetate. When tri-

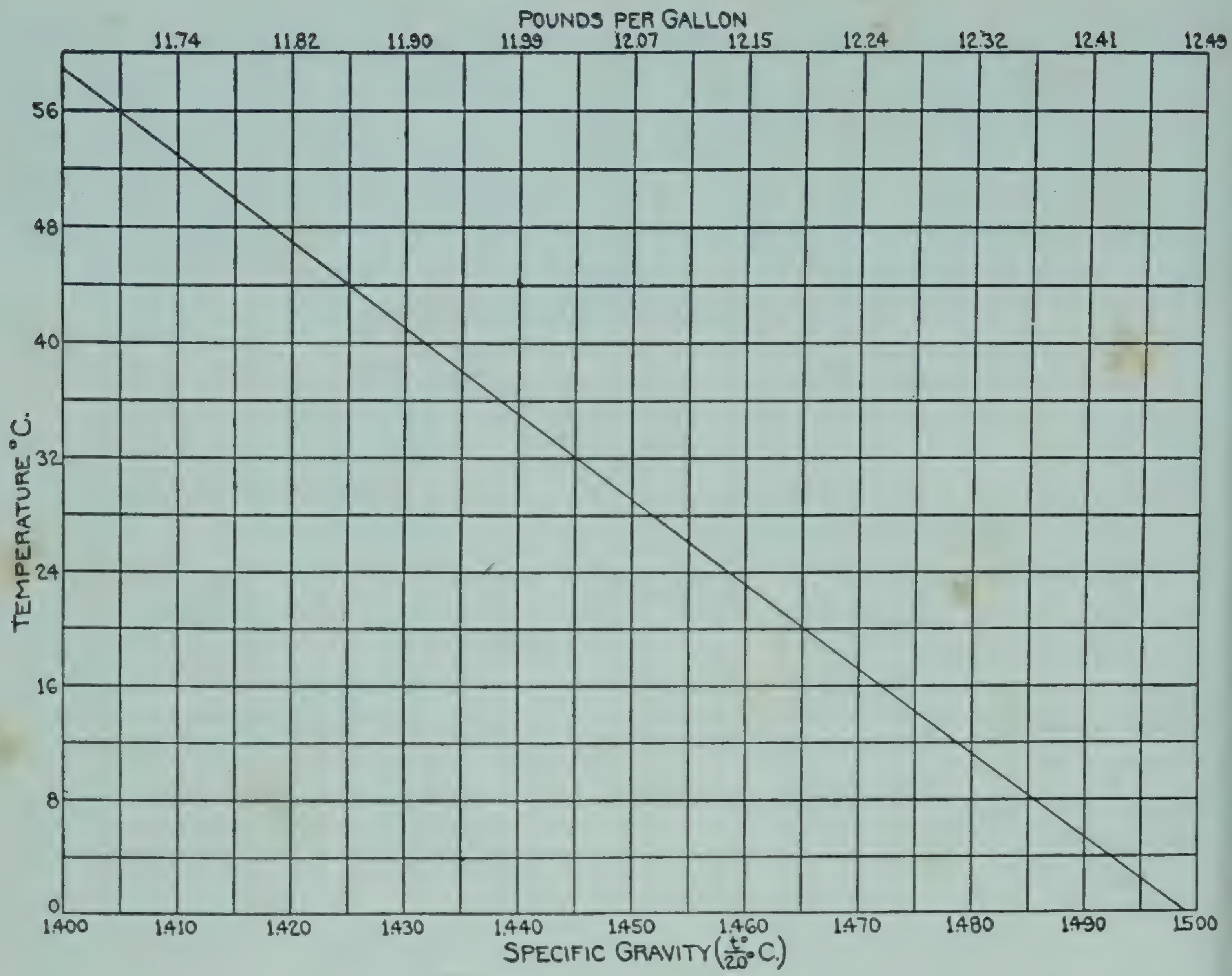


Figure 8.12. Specific Gravity and Weight per Gallon of Trichloroethylene at Various Temperatures.[7]

chloroethylene is mixed with cyclohexanol or *p*-toluene sulfonamide, the mixture is particularly effective with cellulose esters and ethers. It is a solvent for chewing gum, crude rubber, dyes, bitumens, pitch, sulfur, chlorinated hydrocarbons, stearic acid, oils, fats, waxes, grease, tar, gums, caffeine, and such resins as ester gum, rosin, coumarone, mastic, elemi and vinyl.

Trichloroethylene is considered by many the ideal solvent because it so nearly fulfills all the requirements of the perfect solvent, which may be summarized as follows:

High solvent power
Rapid rate of penetration
Ease of separation from extracted matter
Economical recovery
High stability
Low toxicity
Nonflammability
Low specific gravity
Low latent heat of vaporization
Low specific heat
Optimum boiling point

Figure 8.13. Principal Industrial Uses and Applications of Trichloroethylene.[4]

Extraction
Edible Oils
Inedible Oils

Drugs
Purification of Foodstuffs
Purification of Explosives
Recovery of Grease
Analytical Work
Garbage Grease

Degreasing
Metals
Leathers

Raw Wool
Textiles

Machinery
Dewaxing Mineral Oils

Dry Cleaning
Textile Fabrics
Furs

Insecticide Vermicide Fumigant
General Insecticide
Germicidal Soaps
Grape Lice
Mosquitoes
Anthelmintic

Refrigerant
Low Pressure Machines

Preparation of Other Products
Organic Synthesis
Separation of Organic Acids
Soaps
Spotting Preparations
Miscellaneous Preparations

General Solvent
Oils
Fats
Greases
Waxes

Tar

Rubber
Gums
Resins

An extraction medium in many industries, it is used in the extraction and purification of olive, maize, linseed, soybean and other oils from the press cake or native material; of mineral and vegetable waxes, of cocoa butter, fats, nicotine, greases from tankage, bones and leather, and caffeine from coffee. It is recommended and used as a fat solvent in analytical procedures. It is employed as a means of separating formic acid from acetic acid.

As an insecticide, trichloroethylene is used in combination with soap. This mixture destroys the larvae and pupae of such stinging and aquatic insects as mosquitoes and grape lice, and is effective as a disinfectant and cleaner of vermin-infested cloths and floors. It is also used as a fumigant.

It is employed in both the liquid and vapor phase for degreasing metal surfaces, glass, dishes, films, molded articles, leather, textiles, etc. As a cleaning agent, it is used in electroplating metal parts, in the printing, paint, automobile, textile, and leather industries, and in the dry-cleaning industry, where it cleans rapidly, making pre-spotting unnecessary and assuring freedom from fire hazard.

It is also used in making wet soap, neutral and liquid soaps, in egg-covering compounds, in degreasing and depitching compounds, as an ingredient in paint, varnish and tar removers, in household cleaning compounds, in rubber cements, and in shoe and stove polishes. As an intermediate it is used in the manufacture of dyes, pharmaceuticals, perfumes, and organic chemicals. It is a general solvent and laboratory agent and it has wide application as a volatile thinner for paints, lacquers and thermoplastics.

TABLE 8.14. SOLUBILITY OF VARIOUS SUBSTANCES IN TRICHLOROETHYLENE AT 15° C.[4]

(Percentage by Weight as Grams of Substance Dissolved in 100 Grams of Tri)

Material	Per cent by Weight
Benzoic acid	6.9
Boric acid	0.016
Citric acid	0.012
Malic acid	0.01
Salicylic acid	0.28
Tartaric acid	0.005
Adeps suillus	In warm Tri to some degree
Agaricinum	0.014
Aloin	0.013
Amygdalinum	0.029
Anthracene	1.01
Arbutinum	0.011
Asparagin	0.018
Sodium biborate	0.011
Brucine	2.56
Camphor	10 g. dissolve in 5 cc.
Carnauba wax	Well in warm Tri, not so well in cold
Mercuric chloride	0.035
Codeine	12.0
Caffeine	0.76
Colophonium	3 g. dissolve in 5 cc.
Coumarin	1.5 g. dissolve in 5 cc.
Glucose	0.006
Gutta percha	Resinous part easily soluble
Heleninum	1.5 g. easily dissolve in 2 cc.
Codeine hydrochloride	0.014
Mastic	3 g. dissolve in 2 cc.
Nicotine	6.5
Potassium nitrate	0.01
Cocoa butter	Fair
Olive oil	Fair
Piperine	9.83
Saccharine	0.012
Saccharine lactate	0.004
Salicine	0.013
Santonine	2.46
Quinine sulfate	0.07
Sulfur depuratum	1.16
Tannin	0.012
Theobromine	0.008

There are reports that many cellulose acetate silk dyes are soluble in trichloroethylene and show bleeding. The colors which are most affected are the yellows, oranges, reds, and violets. The blues are less affected but the blacks are practically unaffected. The majority of vat dyes are only slightly affected. Indigoid vat dyes bleed more readily than the anthraquinone type. Azoic colors bleed quite badly. However, the following colors show little or no bleeding: basic cotton dyes, basic, acid, direct and mordant silk dyes and sulfur viscose dyes.

TABLE 8.15. EFFECT OF TRI ON TENSILE STRENGTH* OF VARIOUS FABRICS[4]

Values in pounds per inch width

	FILLING		WARP	
	Untreated	Treated with Tri	Untreated	Treated with Tri
Cotton	28.8	27.3	37.2	39.2
Linen	33.3	36.8	39.0	46.2
Silk	22.3	21.2	41.5	43.2
Cellulose acetate Rayon	10.2	10.5	10.8	12.0
Viscose rayon	19.9	20.1	19.3	20.1
Cuprammonium rayon	22.1	21.1	33.2	32.5

* Average of a number of experimental determinations.

Typical Properties and Specifications

Boiling point	86.7°C
Coefficient of expansion per 0°C	0.00115 to 20°C
Dielectric constant, 1000 cycle	3.27
Fire point	Nonflammable
Free chlorine	None
Flash point (A.S.T.M. Open Cup)	None at B.P.
Freezing point	−86.4°C
Latent heat of evaporation at B.P.	57.3 cal./g.
Power Factor, 1000 cycle	2.2%
Specific gravity at 20/20°C	1.4655
Refractive index at 27°C	1.4735
Solubility in water at 25°C	0.10% by wt.
Solubility of water in solvent at 25°C	0.02% by wt.
Surface tension at 25°C	32.0 dynes/cm.
Vapor pressure at −20°C	4.5 mm
−9	9.0
0	17.4
20	56.0
40	145
50	230
65	385
77	562
Viscosity at 25°C	0.00550 poise
Water content	0.002% by wt.
Weight per gallon at 20°C	12.20 lbs.
Acidity calculated as HCl	Not more than 0.001%
Boiling range (760 mm)	95% or better distills from 86.0–87.5°C
Color (Saybolt)	24 max.
Non volatile matter	0.00067% by wt., max.

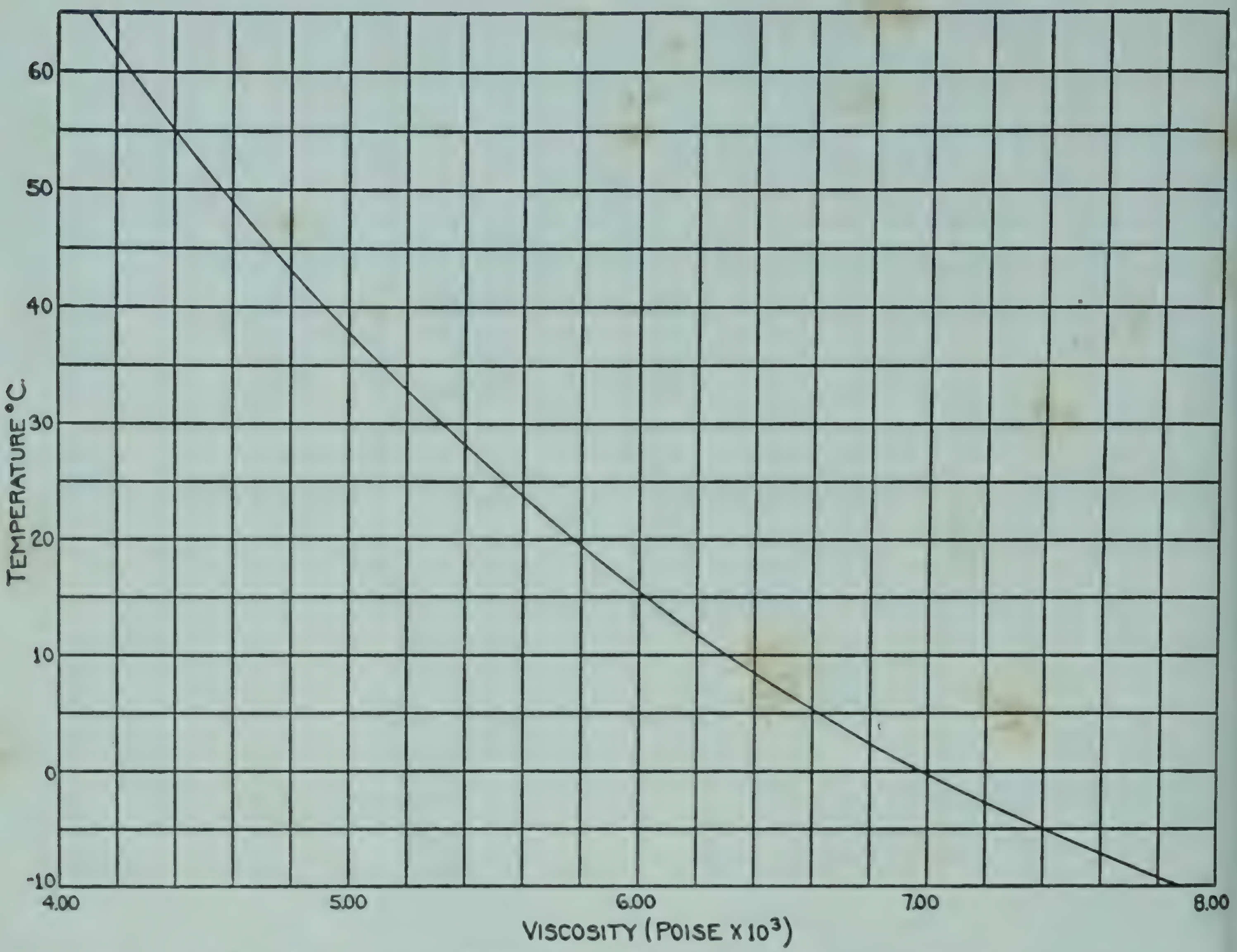


Figure 8.14. Viscosity of Trichloroethylene at Various Temperatures.[7]

Constant-boiling Mixtures

	% by wt.		% by wt.	B.P. (°C)
Trichlorotheylene	84	Allyl alcohol	16	80.9
	88	*tert.*-Amyl alcohol	12	84.0
	86	*tert.*-Butyl alcohol	14	75.0
	92	Isobutyl alcohol	8	85.4
	73	Isopropanol	27	74.0
	64	Methanol	36	60.2
	83	*n*-Propyl alcohol	17	81.7
	93	Water	7	71.8 (742 mm)
Trichloroethylene	69			
Ethanol	26			67.2
Water	5			
Trichloroethylene	81			
n-Propyl alcohol	12			71.5
Water	7			
Trichloroethylene	80			
Allyl alcohol	12			71.4
Water	8			

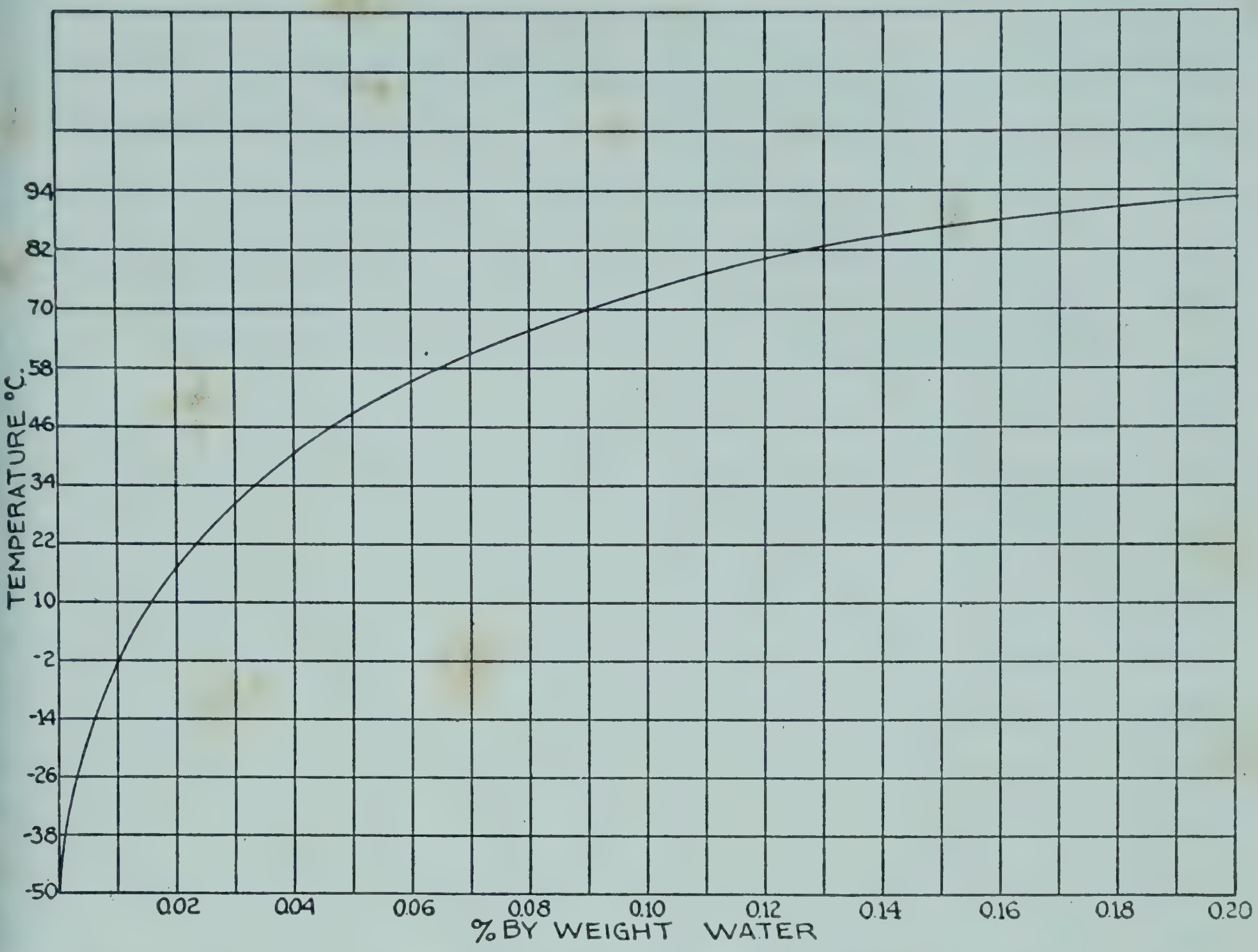


Figure 8.15. Solubility of Water in Trichloroethylene at Various Temperatures.[7]

Trichloroethane (1,1,2-Trichloroethane, Beta-Trichloroethane, Vinyl Trichloride, Ethylene Trichloride) ($Cl\text{-}CH_2CH\text{-}Cl_2$). Trichloroethane is a colorless, volatile liquid, soluble in alcohol, ether, and most organic solvents but difficultly soluble in water. Trichloroethane is stable under ordinary conditions of use and is a good solvent for cellulose acetate and most oils, fats, and waxes, as well as natural rubber and certain types of synthetic rubber. Hence it offers possibilities as an extractant and for other applications that are carried out in closed or well-ventilated systems to prevent toxic quantities of the solvent from being vaporized.

By splitting off hydrogen chloride, trichloroethane is converted to vinylidene chloride, $CH_2{=}CCl_2$, used in the manufacture of resins.

Trichloroethane is classed by the Underwriters' Laboratories standard of classification as nonflammable at ordinary temperatures. Its fire hazard is very small as shown by the following comparative ratings: trichloroethylene, 1; trichloroethane, 3; ethylene dichloride, 60 to 70; gasoline, 90 to 100; ether, 100.

It is volatile and should be used with adequate ventilation to avoid breathing of its vapor. Trichloroethane has a local irritating effect on the

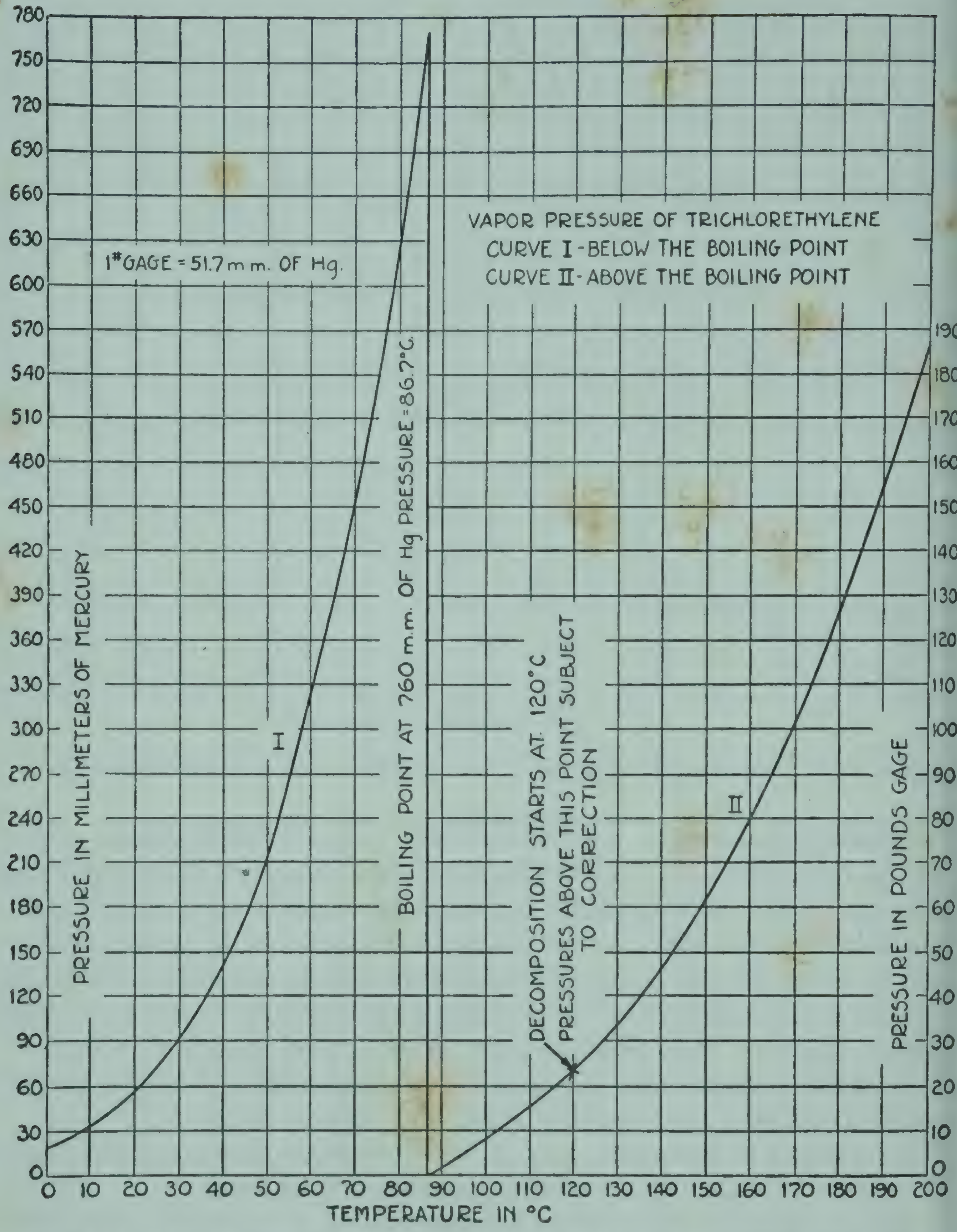


Figure 8.16. Vapor Pressure of Trichloroethylene at Various Temperatures. Curve I, below boiling point. Curve II, above boiling point.[4]

eyes and the mucous membrane of the nose. It is narcotic even in low concentrations. It is less toxic than alpha-trichloroethane, CH_3CCl_3, and tetrachloroethane (acetylene tetrachloride) but more toxic than trichloroethylene, ethylene dichloride, or carbon tetrachloride.

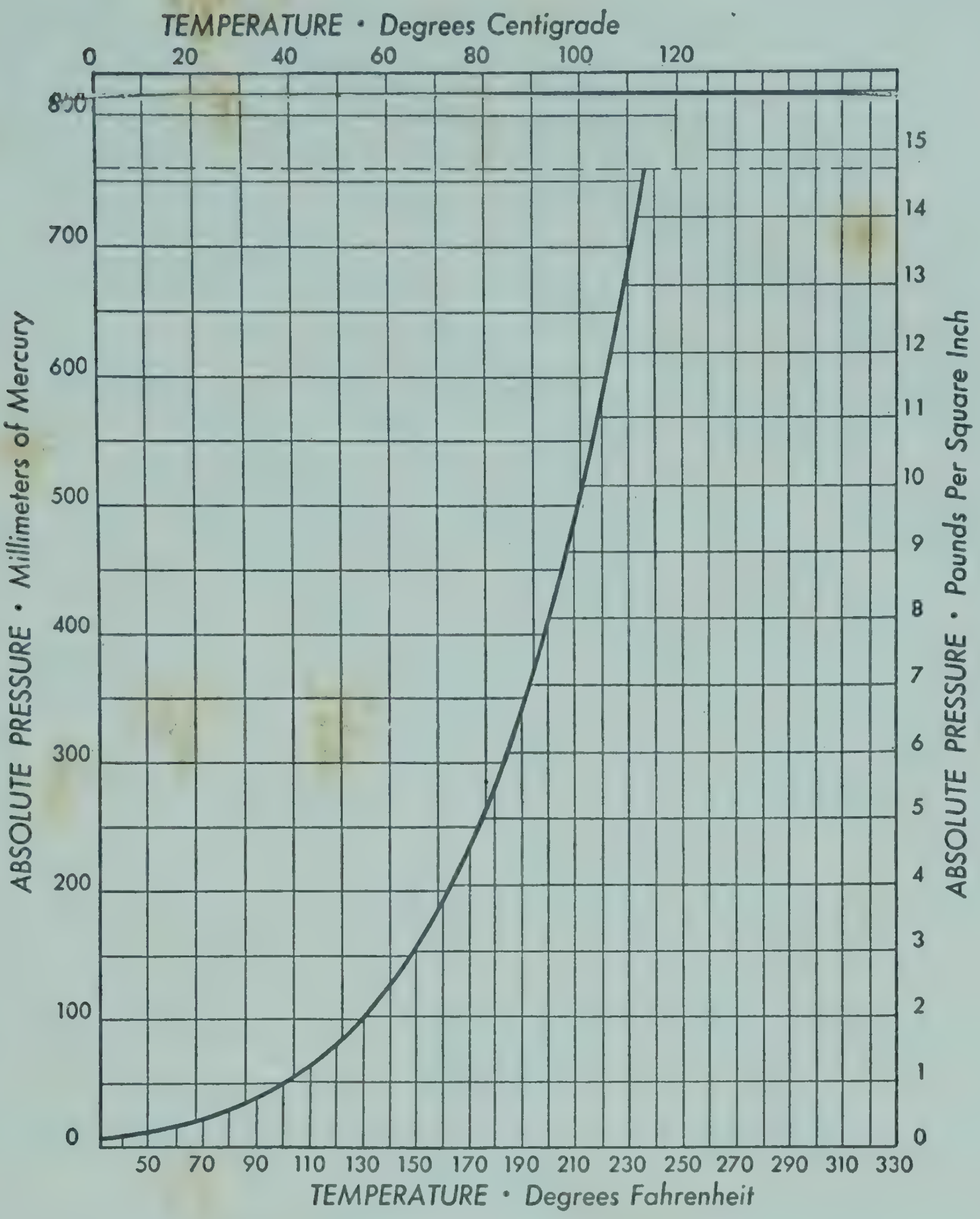


Figure 8.17. Vapor Pressures of Trichloroethane.

Typical Properties and Specifications

Molecular weight	133.4
Specific gravity at 20/20°C	1.4432
Boiling point (760 mm)	113.7°C
Freezing point	−36.7°C
Solubility in water at 20°C	0.45/100 cc
Vapor pressure at 20°C	16.7 mm
Specific heat at 20°C	0.266 cal./g./°C
Weight per gal. at 20°C	12.03 lbs.
Acidity, % as HCl	0.02
Boiling range	110 to 115°C
Color	15 A.P.H.A. units, max.

Tetrabromoethane (Acetylene tetrabromide, 1,1,2,2-tetrabromethane, *sym.*-tetrabromoethane, Múthmann's liquid) ($CHBr_2 \cdot CHBr_2$). Tetra-bromoethane is a nonflammable, heavy, white to yellow, oily liquid with a pleasant characteristic odor. It is sparingly soluble in water but soluble in ethyl alcohol, ethyl ether, chloroform, carbon tetrachloride, and most of

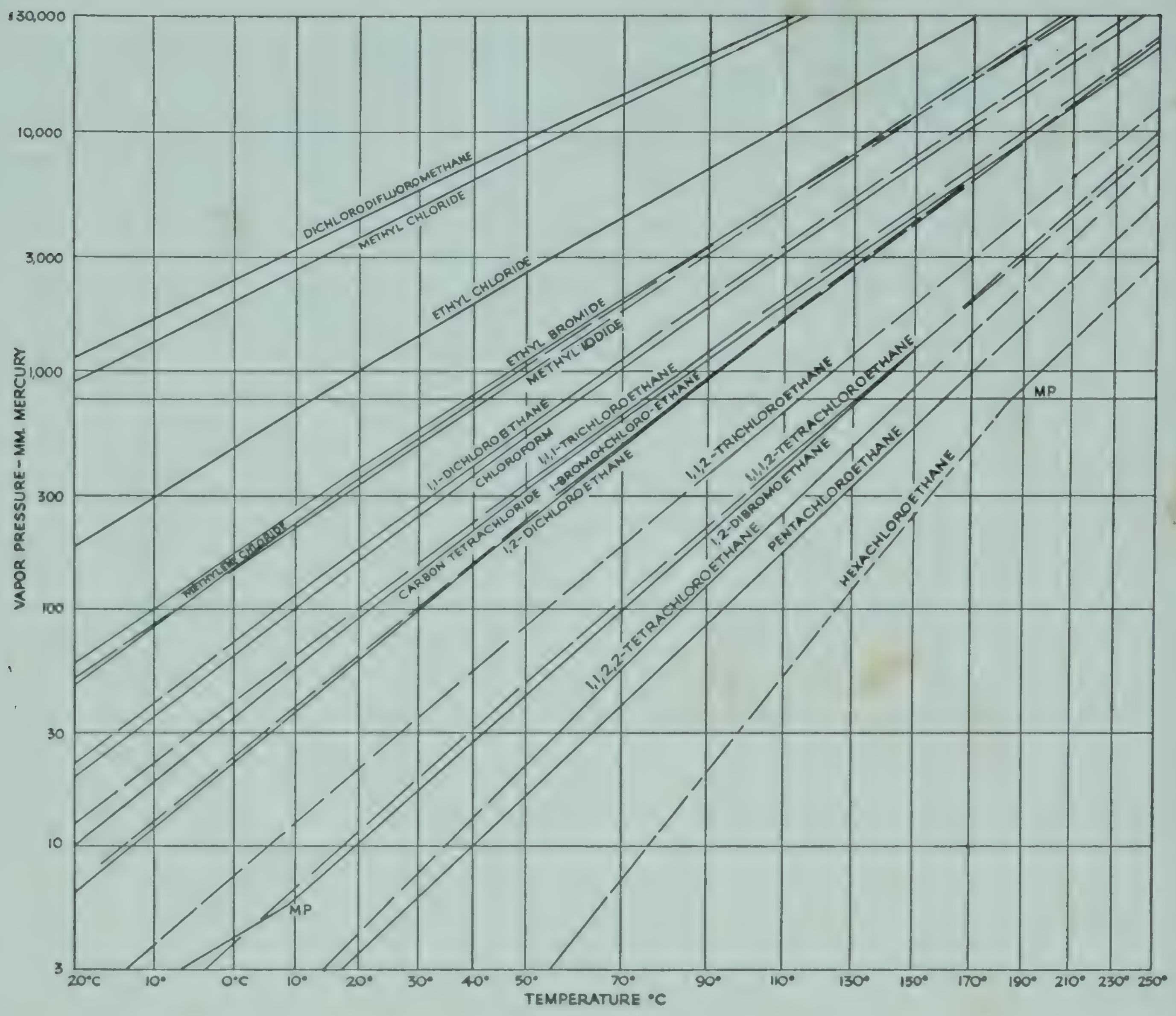


Figure 8.18. Vapor Pressure at Various Temperatures of Some Saturated Halogen Derivatives.*

* Figures 18 and 19 are from a compilation prepared by C. Hadlock, Engr. Dept., E. I. Dupont de Nemours and Co.

the common solvents. It is a good solvent for oils, fats, and waxes. It is used as a solvent, as a fluid in liquid gauges, in microscopy, and in separating mineral mixtures.

Molecular weight	345.7
Boiling point (15 mm)	119°C
Fire point	Nonflammable
Flash point	Nonflammable
Freezing point	−8.3°C
Melting point	0.1°C
Specific gravity at 25/25°C	2.953
Refractive Index	1.637955
Solubility in water at 30°C	0.065 g. per 100 g. solvent
at 80°C	0.28
Weight per gallon at 25°C	24.57 lbs.
Color	Colorless
Purity	Not less than 98%

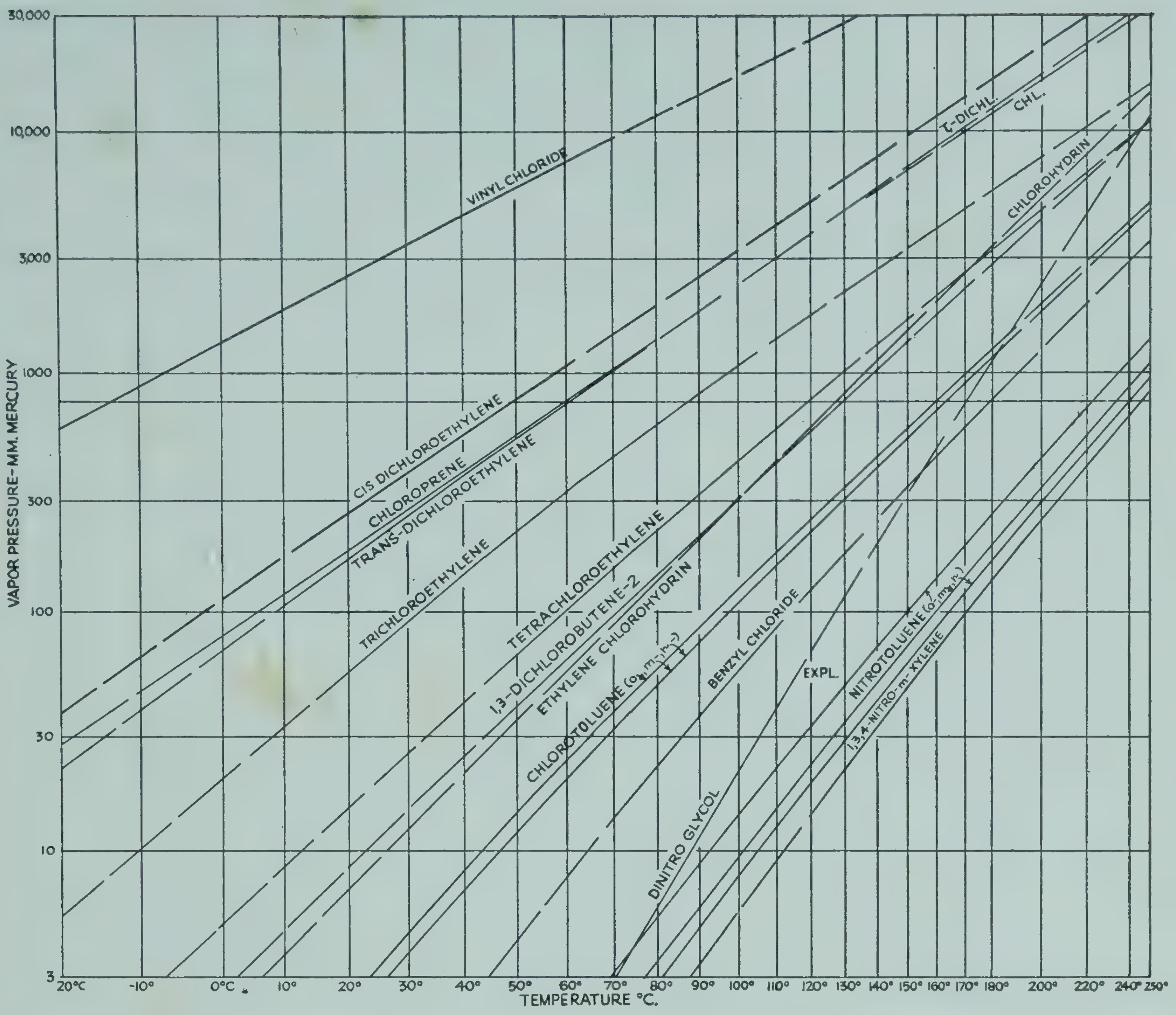


Figure 8.19. Vapor Pressure at Various Temperatures of Unsaturated Aliphatic Halides and Miscellaneous Inorganic Aliphatic and Aromatic Derivatives.

1 ,1 ,2 ,2-Tetrachloroethane (Acetylene tetrachloride, acetosal, boroform, "Cellon") ($CHCl_2$-$CHCL_2$). 1 ,1 ,2 ,2-Tetrachloroethane is a heavy, colorless, mobile liquid which is nonflammable, corrosive, and toxic, and it has a mildly chloroform-like odor. It is made by the chlorination of either ethane, acetylene, or ethylene and has the highest solvent power of the chlorinated hydrocarbons. It is insoluble in water but soluble in ethyl alcohol, ethyl ether, benzene, carbon tetrachloride and many organic solvents and liquids. It dissolves oils, fats, waxes, gums, resins, bitumen, pitch, tarry material, sulfur, phosphorus, halogens, cellulose acetate and nitrate, crude rubber, dyes, camphor, shellac, and many other organic substances. By adding it to a lower aliphatic alcohol or acetate, its solvency for nitrocellulose and cellulose acetate is improved. It is more toxic than chloroform, since contact with its vapors will induce abnormal fatigue and nausea, and prolonged exposure will cause jaundice and enlargement of the liver. Because of its toxicity its commercial applications are limited. It is used, however, in the preparation of varnishes, in mixtures for the removal of paint, varnish, and finishes, in the manufacture of photographic films, lacquers, in smoke-producing compounds, and imitation pearls.

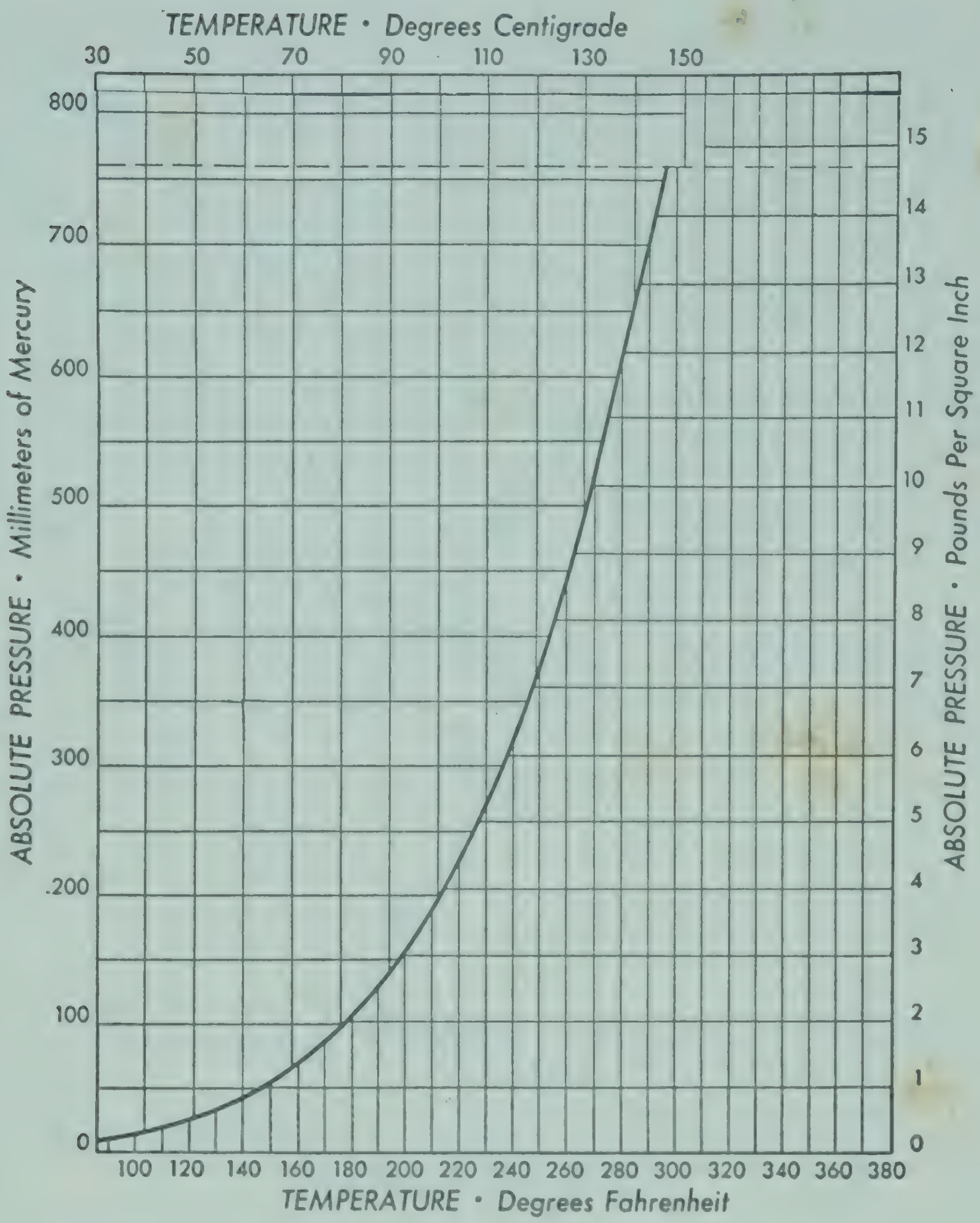


Figure 8.20. Vapor Pressures of Tetrachloroethane.[6]

Typical Properties and Specifications

Molecular weight	167.8
Boiling point	146.5°C
Coefficient of cubical expansions Av./°C Liquid	0.000998 (15–99°C)
Fire point	Nonflammable
Flash point	Nonflammable
Freezing point	−43°C
Heat of vaporization	55.1 cal./g. at B.P.
Specific gravity at 25/25°C	1.593
Specific heat	0.27 cal./gm./°C
Specific resistivity	4.2×10^7 ohms/cm.
Refractive index	1.4942
Solubility in water at 25°C	0.32% by wt.
Solubility of water in solvent at 20°C	0.03% by wt.
Viscosity liquid at 20°C	1.7 centipoises
Vapor pressure at 30°C	9 mm
Water: no cloud at −10°C	0.032% by wt.
Weight per gallon at 25°C	13.25 lbs.
Acidity (ad HCl)	0.0027% by wt. max.
Color	Colorless
Free Halogen	None
Residue on evaporation	0.00062% by wt.

Tetrachloroethylene (Perchloroethylene, tetrachloroethene) $CCl_2{=}CCl_2$). Tetrachloroethylene is a heavy, colorless liquid which is stable, nonflammable, toxic, narcotic, and slightly corrosive to metals. It has an ether-like odor, and is insoluble in water, though soluble in ethyl alcohol, ethyl, ether, benzene, carbon tetrachloride, and most organic solvents. The miscibility and solvency of tetrachloroethylene are similar to those of trichloroethylene, and it is as a substitute for the latter where a slower rate of evaporation is desired. When either of these compounds is mixed with an active solvent, the mixture will dissolve cellulose esters and ethers. It is used as an ingredient in cleaning compounds, dry-cleaning soaps, in fire-extinguishing compounds, as a liquid medium in high tension switches and transformers, and as a general solvent.

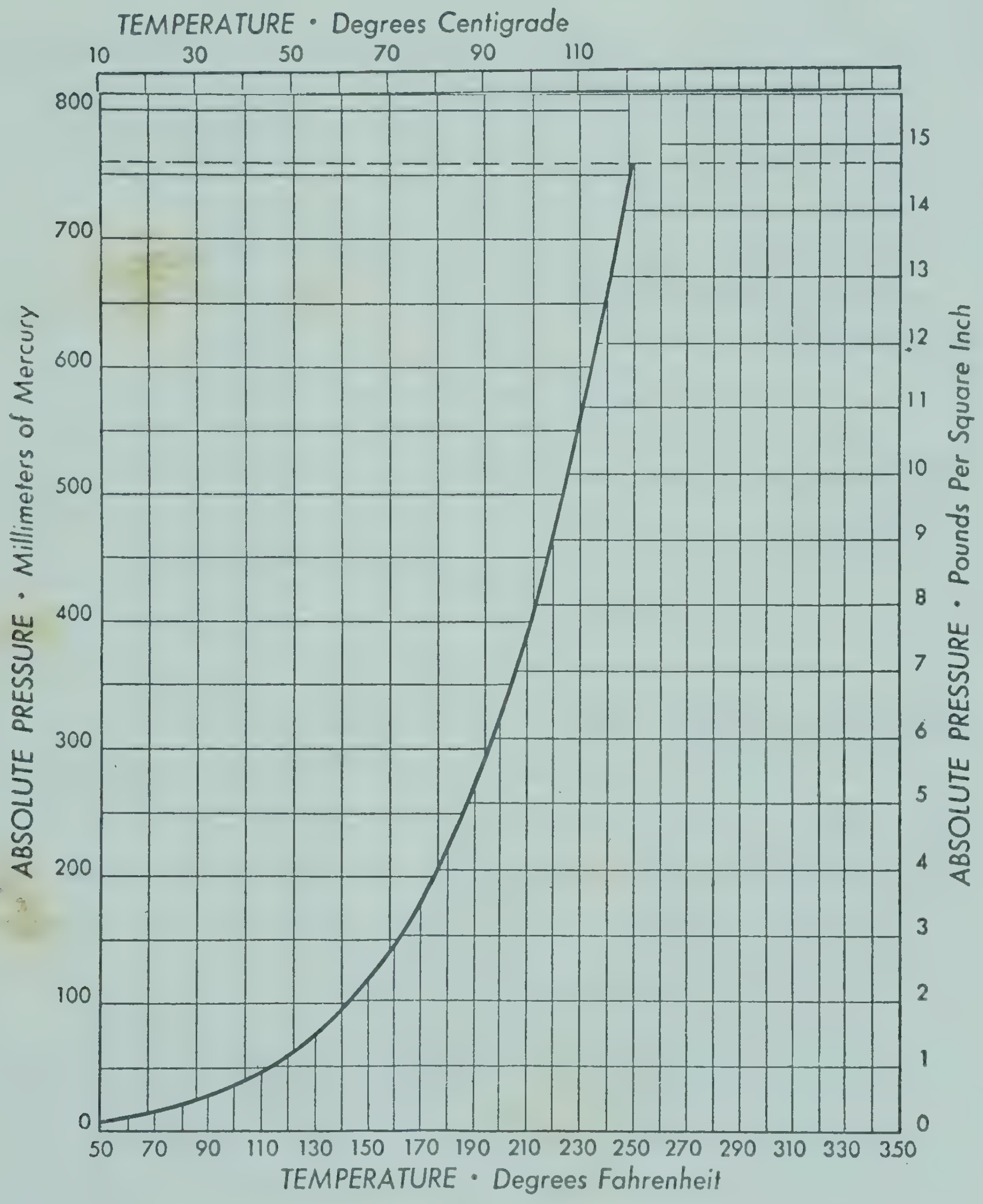


Figure.8.21. Vapor Pressures of Tetrachloroethylene.[4]

Typical Properties and Specifications

Boiling Point	121.0°C
Coefficient of cubical expansion (Av./°C liquid)	0.001079 (15–90°C)
Dielectric constant, 1000 cycle	2.20
Dielectric strength, 0.1° gap	30,000 volts
Explosive limits	None
Fire point	Nonflammable
Flash point	Nonflammable
Freezing point	−22.4°C
Latent heat of evaporation at B.P.	50.1 cal./g.
Power factor, 1000 cycle	0.02%
Residue on evaporation	0.0106% by wt., max.
Specific gravity at 25/25°C	1.618
Specific heat	0.21 cal./g./°C
Specific resistivity	1.8x10^{13} ohms/cm.
Refractive Index	1.5055
Solubility in water at 25°C	0.04% by wt.
Solubility of water in solvent at 20°C	0.02% by wt.
Vapor pressure at 30°C	28 mm
Viscosity at 20°C	0.90 centipoise
Water content	0.008% by wt.
Weight per gallon at 25°C	13.46 lbs.
Acidity (as HCl)	0.001% by wt., max.
Boiling Range (760 mm)	120–122°C
Color (Saybolt)	No. 22
Non-volatile matter	0.0007% by wt. max.

Pentachloroethane ($CHCl_2CCl_3$). Pentachloroethane is a heavy, colorless, nonflammable, toxic liquid made by chlorinating tetrachloroethane or trichloroethylene. This high-boiling solvent is stable in the absence of water. It is a good solvent for vegetable, mineral and essential oils, gum, resins such as dammar, elemi, mastic and sandarac, and for cellulose acetate and some types of cellulose ethers. Since its physical and chemical properties and solvent power are similar to the more toxic tetrachloroethane it may be substituted for the latter in most industries. The solvent mixtures for cellulose acetate which have been suggested by Lindsay are made up of some 200 combinations containing pentachloroethane.

Typical Properties and specifications

Boiling point (760 mm)	161.9°C
Coefficient of cubical expansion Av/°C liquid	0.0009097
Explosion limits	None
Flash point	Nonflammable
Freezing point	−22.0°C
Latent heat of vaporization (at B.P.)	43.6 cal.g. 78.4 B.t.u./lb.
Specific gravity at 20.4°C	1.678
Specific heat at 20°C (liquid)	0.215 cal./g./°C

Refractive index	1.5035
Solubility in water at 25°C	0.05 g./100 g.
Solubility of water in solvent at 20°C	0.24 g. water/100 g.
Vapor density (at B.P. and 760 mm)	5.68 g./liter
Vapor pressure at 30°C	6 mm
Viscosity liquid at 20°C	2.45 centipoises
Weight per gallon at 20°C	14.00 lbs.
Acidity as HCl	0.001% by wt., max.
Color (Saybolt)	18 max.
Free halogen	None
Non-volatile matter	0.0007% by wt., max.

Hexachloroethane (Perchloroethane, carbon trichloride, tetrachloroethylene dichloride) (CCl_3CCl_3). Hexachloroethane is a nonflammable, white to slightly yellow crystalline compound with a camphor-like odor. It is insoluble in water but soluble in ethyl alcohol, ethyl ether, and oils. It is used in the manufacture of synthetic organic chemicals and in smoke screen manufacture.

Typical Properties and Specifications

Boiling point (760 mm)	Sublimes at 185°C
Latent heat of vaporization at B.P.	46.4 cal./g. 83.5 B.t.u./lb.
Melting point in sealed tube	188.2°C
Specific gravity at 20/4°C	2.091
Specific heat at 25°C	0.174 cal./g./°C or B.t.u./lb./°F
Vapor density at B.P. and 760 mm	6.30 g./liter
Vapor pressure at 30°C	2 mm
Water	0.2% by wt., max.
Acidity (as HCl)	Less than 0.05%
Nonvolatile matter	less than 0.15%
Purity	98.0%, min.

Isopropyl Chloride ($CH_3CHClCH_3$). Isopropyl chloride is a clear, colorless liquid with an ethereal odor. It is miscible with alcohol and ether but only slightly soluble in water. It is used in the manufacture of thymol and in organic synthesis.

Boiling point	35.4°C
Freezing point	−117°C
Specific gravity at 20/4°C	0.8590 g./100 g.
Refractive index	1.3811
Solubility in water at 12.5°C	0.344
Viscosity at 22.50°C	0.2962 centipoise
Weight per gallon	7.5 lbs.

Allyl Chloride (3-Chloropropene-1) ($CH_2{:}CH{\cdot}CH_2Cl$). Allyl chloride is a water-white, volatile liquid of mild odor. It is insoluble in water but solu-

TABLE 8.16. CHLORINATED HYDROCARBONS

Physical Properties

	Methyl Chloride	Methylene Chloride	Chloroform Tech. 98%	Carbon Tetrachloride	Dichlorethylene "Di-48"	Dichlorethylene "Di-60"	*Dichlorethylene "48-60"	Trichlorethylene	Perchlorethylene
Chemical Formula	CH_3Cl	CH_2Cl_2	$CHCl_3$	CCl_4	HCl C=C ClH	HH C=C ClCl	CHCl= CHCl	CHCl= CCl_2	CCl_2= CCl_2
Molecular Weight	50.48	84.93	119.37	153.83	96.93	96.93	96.93	131.38	165.83
Boiling Point at 760 mm. Hg. (° C.)	−23.7	39.8	61.2	76.7	48.4	60.3	48.4–60.3	86.7	120.8
(° F.)	−10.7	103.6	142.2	170.1	119.1	140.5	119.1–140.5	188.1	249.4
Freezing Point (° C.)	−97.6	−96.7	−63.2	−23.0	−50.0	−80.5	−50.0−−80.5	−88.0	−22.4
(° F.)	−143.7	−142.1	−81.7	− 9.4	−58.0	−112.9	−58.0−−112.9	−126.4	− 8.3
Latent heat of cal./g.	102.4	75.3	59.0	46.5	73.7	73.0	73.3	57.3	50.1
Vaporization (at B.P.) B.t.u./lb.	184.3	135.5	106.1	83.7	132.6	131.3	131.8	103.1	90.1
Specific Heat at 20° C. (Liquid) cal./g./° C. or B.t.u./lb./° F.	0.382	0.289	0.234	0.201	0.270	0.270	0.270	0.223	0.216
Specific Gravity at 20/4° C.	1.002 at −23.7° C.	1.336	1.489	1.595	1.257	1.282	1.272	1.462	1.623
Pounds per Gal. at 20° C.	8.34 at −23.7° C.	11.15	12.43	13.31	10.49	10.70	10.61	12.20	13.55
Vapor Density g./liter	2.47	3.32	4.36	5.37	3.67	3.54	—	4.45	5.13
(at B.P. and lb./cu. ft.	0.154	0.206	0.272	0.335	0.230	0.221	—	0.278	0.320
760 mm.) air=1.00	1.74	2.94	4.13	5.32	3.34	3.35	—	4.53	5.72
Solubility in Water at 25° C. g./100 g.	0.48	2.11	0.88	0.09	0.63	0.77	0.75	0.17	0.04
Refractive Index (20° C.)	—	1.4237	1.4467	1.4607	1.4490 at 15° C.	1.4519 at 15° C.	1.4507 at 15° C.	1.4777	1.5055
Vapor Pressure at 30° C. 760 mm. Hg.	4940	511	246	141	383	255	306	94	33
Inflammable	Mod.	No	No	No	Mod.	Mod.	Mod.	No	No
Specifications‡	**								
Boiling Range, 760 mm. Hg. (° C.)	−24.6 to −23.6	39.2 to 40.0	60.0 to 61.5	76.2 to 77.0	47.0 to 48.5	57.5 to 61.0	51.0 to 61.0	86.0 to 87.5	120.0 to 122.0
No cloud at:		−24° C.	−10° C.		−15° C.	−15° C.	−15° C.	−10° C.	0° C.
Max. Water, % by wt.	0.008	0.027	0.021		0.004	0.001	0.004	0.002	0.008
Mac. Acid (as HCl), % by wt.	0.001	0.001	0.001	None	0.0005	0.0005	0.0005	None	0.001
Max. Residue, % by wt.	0.01	0.00075	—	0.0015	0.0007	0.0007	0.0007	0.002	0.0007
Specific Gravity, (15/4° C.)		1.333 to 1.336	1.478 to 1.482 at 25/4° C.	1.595 to 1.597 at 20/15.5 ° C.	1.261 to 1.266	1.288 to 1.293	1.279 to 1.285	1.472 to 1.476	1.628 to 1.632
Maximum Color	Water-White	Saybolt No. 24	Saybolt No. 24	Clear Colorless	Saybolt No. 24	Saybolt No. 24	Saybolt No. 24	Saybolt No. 24	Saybolt No. 22

***Mixture of 40% by weight of "Di-48" and 60% by weight of "Di-60."**

****Methyl Chloride or ARTIC is supplied according to these specifications as well as under two additional formulas, namely, "A" and "N". These products are prepared by adding from 0.3 to 1.3% by weight of a warning agent to the original material. These addition agents produce variations in the properties of the original material, particularly in its odor and color.**

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TABLE 8.16. CHLORINATED HYDROCARBONS—*Continued*

Physical Properties

	Ethyl Chloride	Ethylene Dichloride	Beta-Trichlor-ethane	Tetrachlor-ethane	Pentachlor-ethane	Hexachlor-ethane	Propylene Dichloride
Chemical Formula	CH_3-CH_2Cl	CH_2Cl-CH_2Cl	$CH_2Cl-CHCl_2$	$CHCl_2-CHCl_2$	$CHCl_2-CCl_3$	CCl_3-CCl_3	$CH_3CHCl-CH_2Cl$
Molecular Weight	64.50	98.95	133.40	167.85	202.29	236.75	112.96
Boiling Point at 760 mm. Hg. (° C.)	12.5	83.7	113.5	146.3	161.9	Sublimes at 185° C. or 365° F.	95.9
(° F.)	54.5	182.7	236.3	295.3	323.4		204.6
Freezing Point (° C.)	−138.7	−35.3	−36.7	−43.8	−22.0		−80
(° F.)	−217.7	−31.5	−34.1	−46.8	−7.6		−112
Latent Heat of Vaporization (at B.P.) cal./g.	93.0	77.4	68.7	55.2	43.6	46.4	79
B.t.u./lb.	167.3	139.2	123.6	99.3	78.4	83.5	142
Specific Heat at 20° C. (Liquid) cal./g./° C. or B.t.u./lb./° F.	0.394	0.301	0.266	0.269	0.198	0.174 at 25° C.	0.31
Specific Gravity at 20/4° C.	0.921 at 0° C.	1.257	1.441	1.595	1.678	2.091	1.155
Pounds per Gal. at 20° C.	7.69 at 0° C.	10.49	12.04	13.31	14.00	—	9.64
Vapor Density (at B.P. and 760 mm.) g./liter	2.76	3.88	4.21	4.88	5.68	6.30	3.72
lb./cu. ft.	0.172	0.211	0.263	0.305	0.355	0.393	0.232
air = 1.00	2.24	3.92	4.61	5.79	7.02	8.20	3.90
Solubility in Water at 25° C. g./100 g.	0.20 at 11° C.	0.89	0.48	0.32	0.05	—	0.27
Refractive Index (20° C.)	1.1179 at 0° C.	1.4443	1.4711	1.4942	1.5035	—	1.4418
Vapor Pressure at 30° C. 760 mm. Hg.	1400	100	35	7	6	0.5	67
Inflammable	Yes	Mod.	No	No	No	No	Mod.

Specifications‡

	Ethyl Chloride	Ethylene Dichloride	Beta-Trichlor-ethane	Tetrachlor-ethane	Pentachlor-ethane	Hexachlor-ethane	Propylene Dichloride
Boiling Range, 760 mm. Hg. (° C.)	95% 12.0 to 13.0	† 82.1 to 84.6	111.0 to 115.0	—	—	—	† 94.4–97.0
No cloud at:	−15° C.		−15° C.	−10° C.	−10° C.		
Max. Water, % by wt.	0.011	0.092	0.016	0.023	0.001	—	0.038
Max. Acid (as HCl), % by wt.	0.001	—	0.0005	0.0027	0.001	0.05	1.00
Max. Residue, % by wt.	0.01	0.0009	0.0008	0.0007	0.0007	0.15	0.002
Specific Gravity, (15/4° C.)	0.922 to 0.925 at 0/4° C.	1.252 at 20/20° C.	1.446 to 1.452	1.598 to 1.602	1.683 to 1.690		1.161 at 20/20° C.
Maximum Color	Water-White		Saybolt No. 24	Saybolt No. 18	Saybolt No. 18		

†Representative analyses of Ethylene Dichloride and Propylene Dichloride.

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ble in ethyl alcohol, ethyl ether, and carbon tetrachloride. It is used in the manufacture of pharmaceuticals and in the synthesis of numerous allyl derivatives.

Boiling point	45°C
Fire point	4°C
Flash point	4°C
Latent heat of vaporization	84.6 cal./g.
Specific gravity at 25/25°C	0.933
Specific heat	0.31 cal./g./° C
Refractive index at 25°C	1.412
Viscosity at 25°C	0.33 centipoise
Weight per gallon at 25°C	7.8 lbs.

Propylene Dibromide (1,2-Dibromopropane, propylene bromide) ($CH_3CHBrCH_2Br$). Propylene dibromide is a heavy, water-white liquid, with a sweet odor. It is only slightly soluble in water but is soluble in ethyl alcohol, ethyl ether, acetone, benzene and carbon tetrachloride. It is used in organic synthesis.

Boiling range, 5–95%	139.6–142.6°C
Fire point	Nonflammable
Flash point	Nonflammable
Specific gravity at 25/25°C	1.943
Refractive index at 25°C	1.519
Solubility in water at 25°C	0.2% by wt.
at 80°C	0.3% by wt.
Weight per gallon at 25°C	16.2 lbs.

Propylene Dichloride (1,2-Dichloropropane, propylene chloride) ($CH_3CHClCH_2Cl$). Propylene dichloride is a stable, colorless liquid with a characteristic odor. It has a low flammability but it can be made nonflammable by adding 25 per cent by volume of carbon tetrachloride. Its odor and solvent properties resemble those of ethylene dichloride. It is soluble in ethyl alcohol, ethyl ether, benzene, carbon tetrachloride, and most organic solvents. It is a solvent for oils, fats, waxes, gums, and resins, and some dyes. When an active solvent like acetone is added, propylene dichloride becomes a solvent for cellulose esters and ethers. Because of its wide range of solvency, its low specific gravity and its stability, it is a desirable solvent in many industries. It is used as an intermediate in the synthesis of amines and rubber chemicals, as an inert reaction medium for chlorination and sulfonation, as an ingredient in dry-cleaning fluids, scouring compounds and spotting agents. It is also used as a soil fumigant and insecticide.

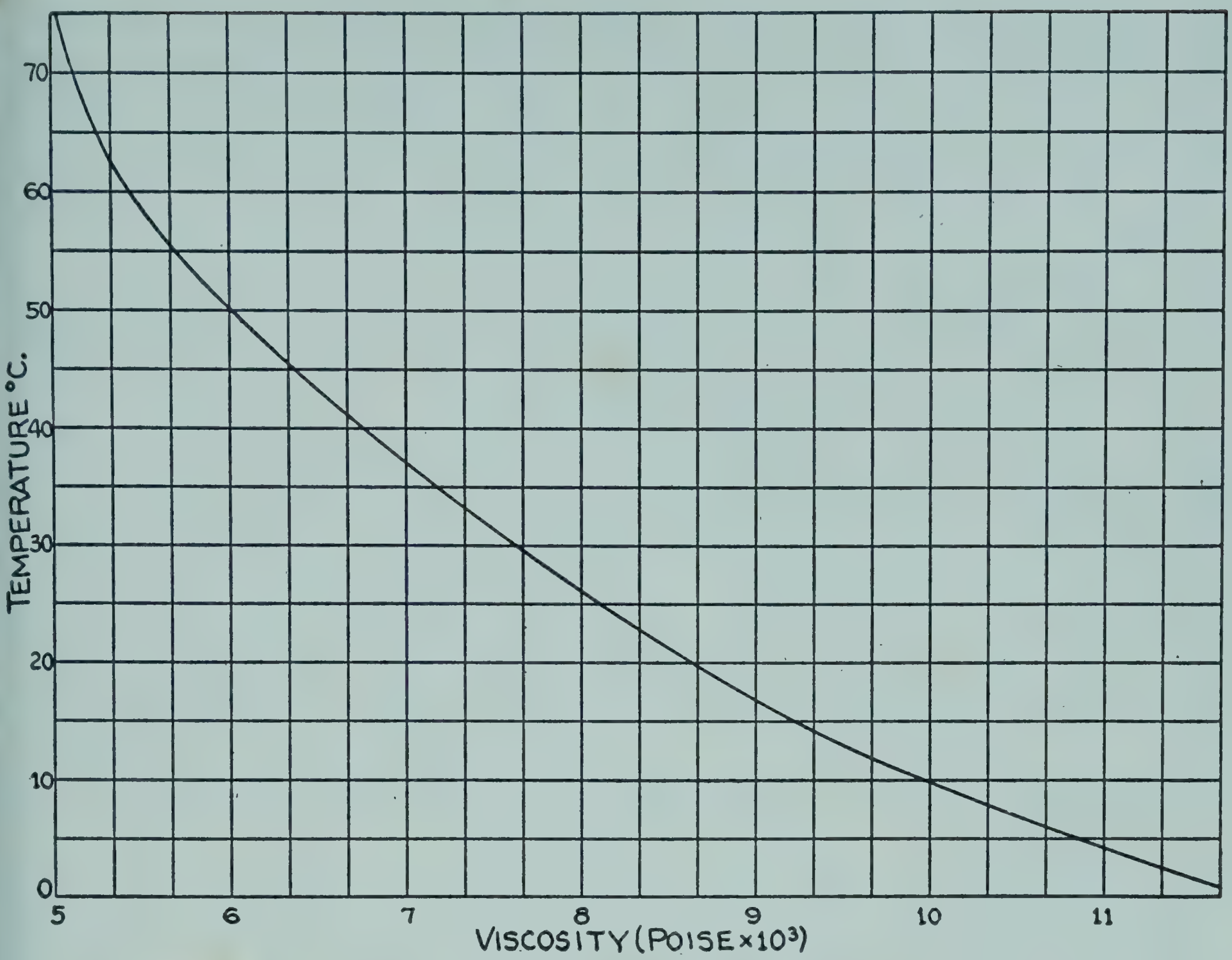


Figure 8.22. Viscosity of Propylene Dichloride at Various Temperatures.[7]

Typical Properties and Specifications

Boiling point	95.9°C
Coefficient of expansion (per°C)	0.001108 to 20°C 0.001153 to 55°C
Dielectric constant (85.8 kilocycles)	8.925 recip. ohms at 26°C
Explosive limits in air	Lower = 3.4% by vol. at 25°C Upper = 14.5% by vol. at 100°C
Flash point (A.S.T.M. open cup)	21°C
Freezing point	−70°C
Ignition temperature in air	557°C
Latent heat of vaporization at B.P.	72.2 cal./g.
Specific gravity at 20/20°C	1.157 to 1.163
Specific heat (liquid) at 20°C	0.31 cal./g./°C or B.t.u./lb./°F
Refractive index	1.4418
Solubility in water at 20°C	0.26% by wt.
Solubility of water in solvent at 20°C	0.07% by wt.
Surface tension at 25°C	31.4 dynes/cm.
Vapor density (at B.P. and 760 mm)	3.72 g./liter
Vapor pressure at 20°C	35.8 mm
Viscosity at 20°C	0.00865 poise
Weight per gallon at 20°C	9.65 lbs.
Acidity (as HCl)	0.005% max.
Boiling range (760 mm.)	93–99°C
Color	Water-white
Free halogen	None
Non-volatile Matter	0.005 g./100 cc., max.

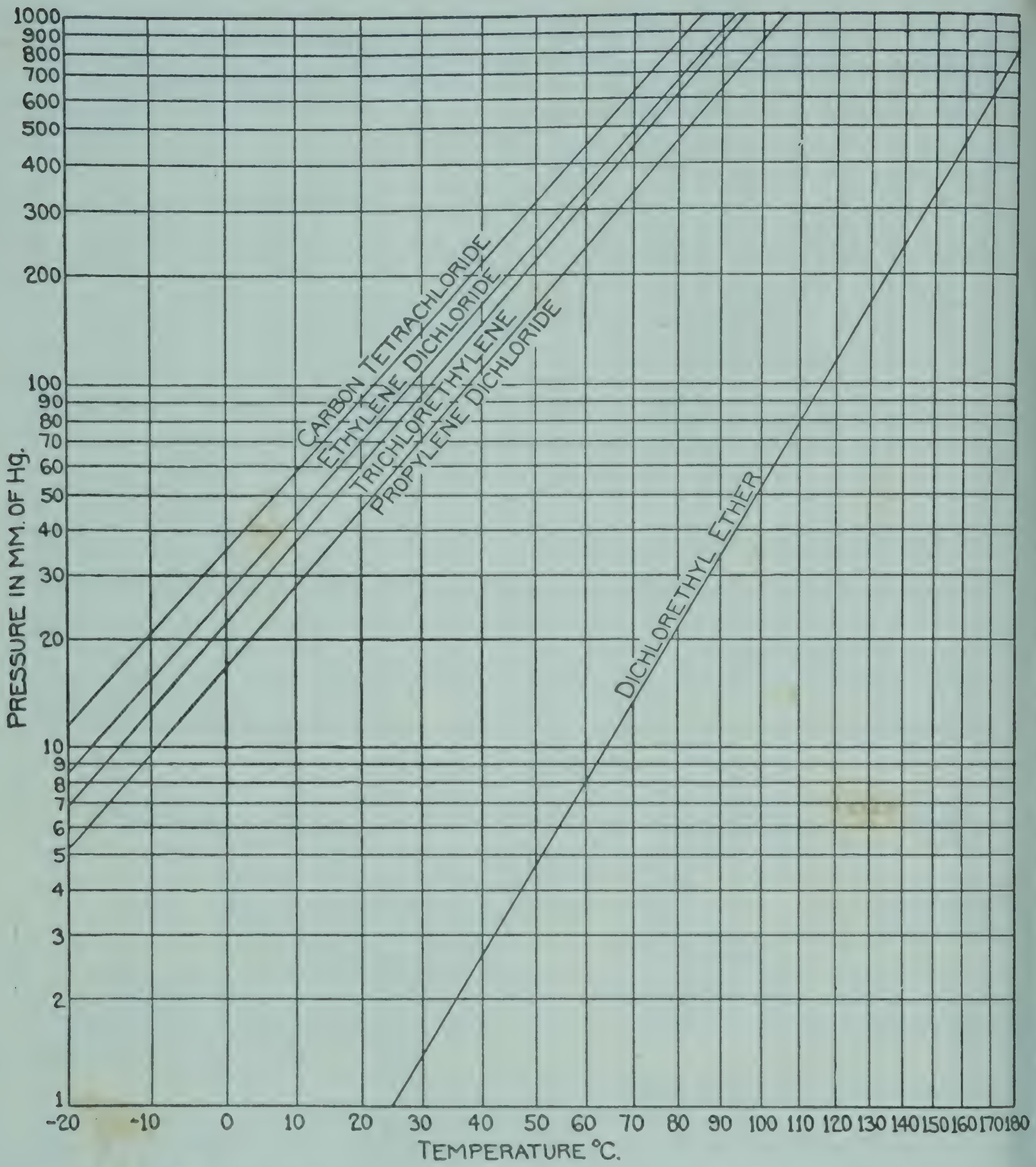


Figure 8.23. Vapor Pressure of Various Chlorinated Solvents at Different Temperatures.[7]

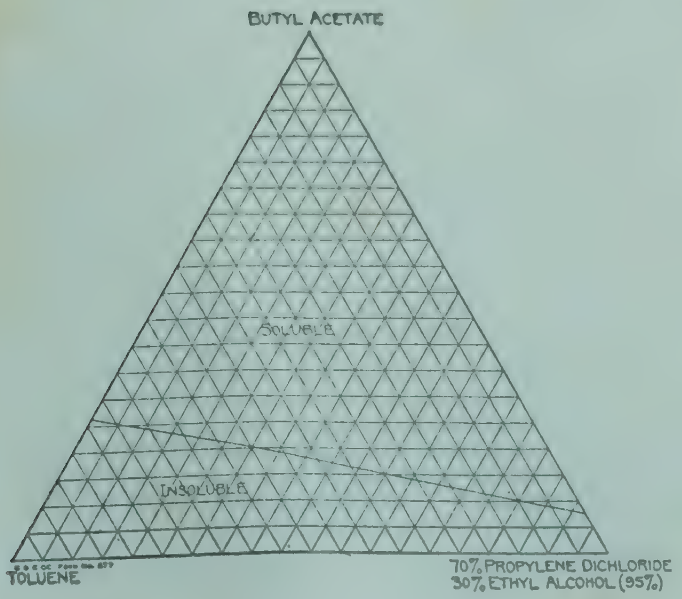


Figure 8.24.

Solubility of ½-Sec. R. S. Nitrocellulose in Mixtures of Butyl Acetate, Toluene and 70-30 Propylene Dichloride-Alcohol.

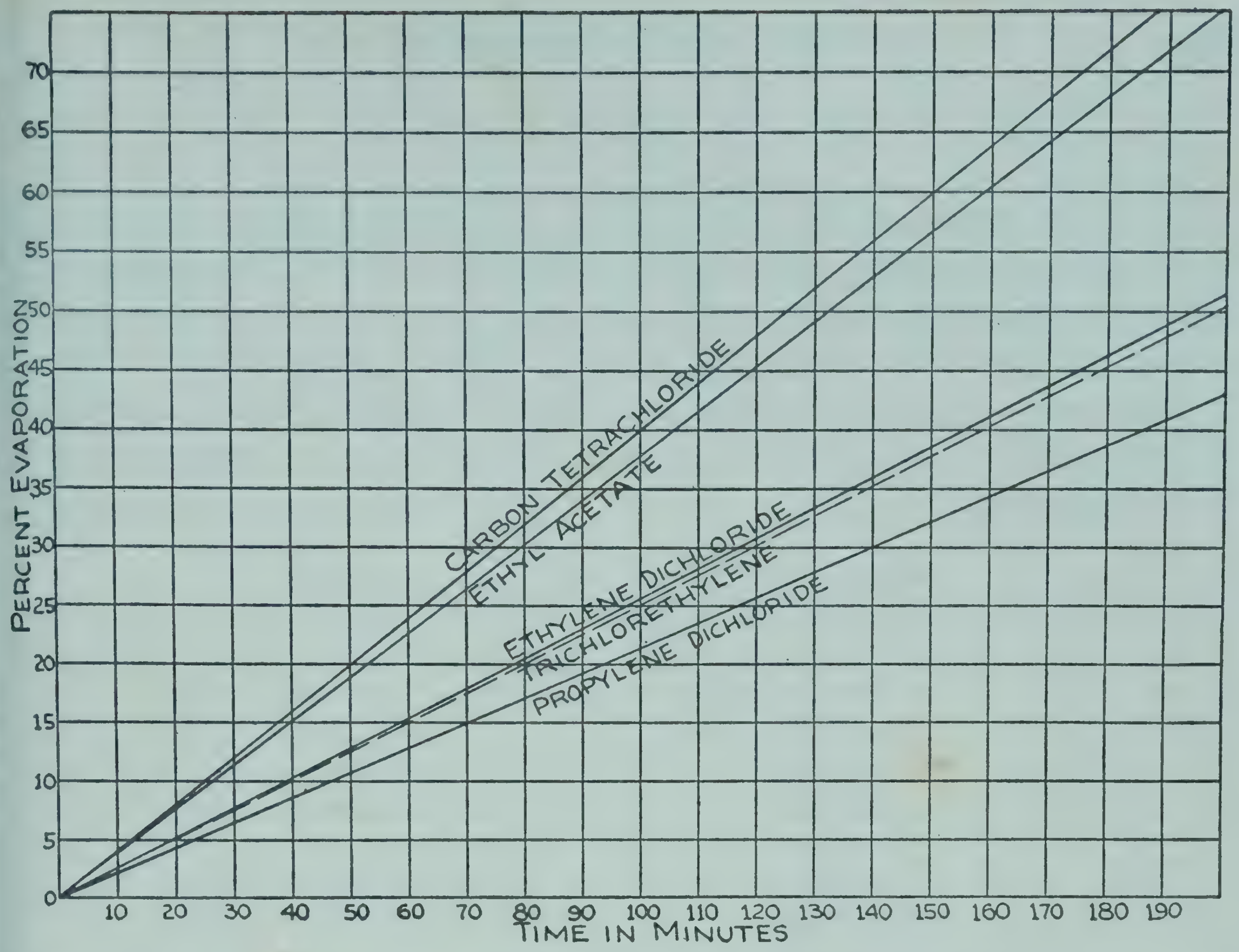


Figure 8.25. Evaporation Rate of Ethyl Acetate and Various Chlorinated Solvents at Room Temperature.[7]

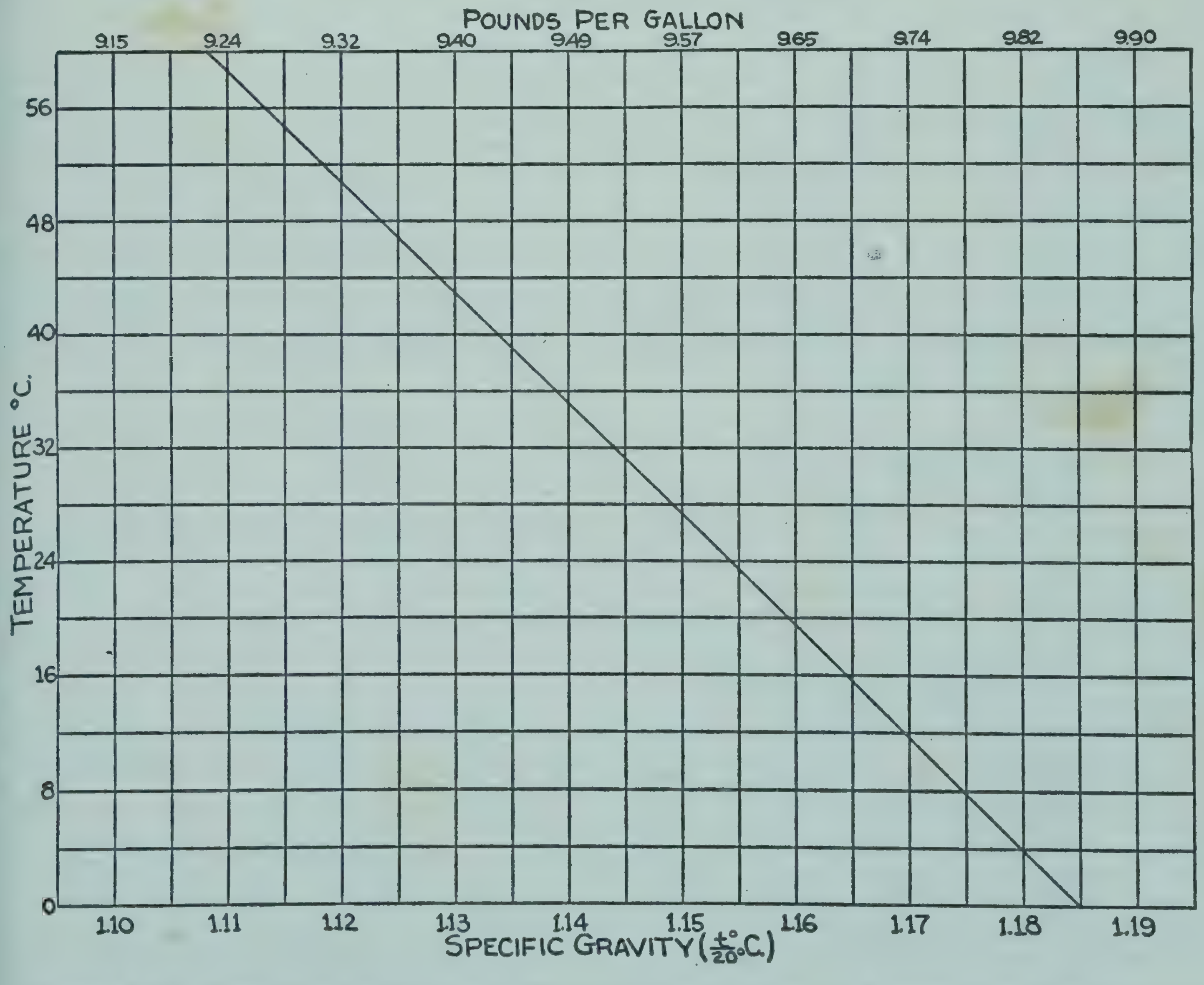
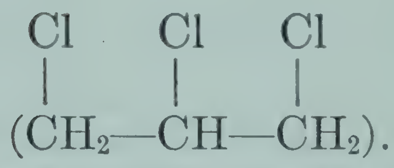


Figure 8.26. Specific Gravity and Weight Per Gallon of Propylene Dichloride at Various Temperatures.[7]



Trichloropropane ($CH_2—CH—CH_2$, each carbon bearing Cl). 1,2,3-Trichloropropane has recently been announced as being available in commercial quantities.[8] It is claimed to have high solvency for oils, fats, waxes, chlorinated rubber and numerous natural and synthetic resins. Its low evaporation rate indicates possible use in paint and varnish removers and engine-cleaning compounds. It is reasonably nonflammable and will not ignite at any temperature below its boiling point.

Molecular weight	147.44
Specific gravity, 20/20°C	1.385
Color, Pt-Co	15
Refractive index	1.4832
Distillation range, °C	
IBP	150
90%	156.1
95%	156.1
DP	156.6
Flash point	165°F
Analysis, % W	
Trichloropropane	97.0
Epichlorohydrin	1.5
Glycerol dichlorohydrin	1.5

n-**Butyl Chloride** (1-Chlorobutane) ($CH_3CH_2CH_2CH_2Cl$). Normal butyl chloride is a water-white liquid insoluble in water but soluble in methyl and ethyl alcohol, ethyl ether, ethyl acetate, acetone, aromatic and aliphatic hydrocarbons, fixed oils, mineral oil, oleic and hot stearic acids and hot paraffin and carnauba waxes, the latter two congealing when cooled. It is used as a solvent and in organic synthesis particularly as a butylating agent for introducing the butyl group into different organic compounds, and as an anthelmintic.

Boiling point (760 mm)	78°C
Distillation range	Not less than 95% between 76.0–79.5°C
Flash point (Open cup)	20°F
Latent heat of vaporization at 76.5°C	79.8 cal./g.
Melting point	−123.1°C
Specific gravity at 20/4°C	0.884
Specific heat at 20°C	0.451 cal./g.
Refractive index at 20°C	1.4004
Surface tension at 20°C	23.66 dynes/cm.
Solubility in water	Negligible
Water content	None
Weight per gallon	7.37 lbs.
Acidity	0.01% max.
Color	Water-white

Mixed Amyl Chlorides ($C_5H_{11}Cl$). This product is believed to be a mixture of all the monochlorides of normal and isopentane. They form a straw to purple-colored liquid, insoluble in water, but soluble in methyl alcohol, ethyl ether, acetone, ethyl acetate, aromatic and aliphatic hydrocarbons, fixed oils, mineral oil, oleic and hot stearic acids, and hot paraffin and carnauba waxes, the latter two congealing when cooled. The product is used mainly for the synthesis of amyl compounds, but it may be used as a solvent, in rotogravure inks, and for soil fumigation when combined with the dichloropentanes.

Typical Properties and Specifications

Boiling point (approximate)		
1-Chloropentane		108.2°
2-Chloropentane		96.7
3-Chloropentane		97.3
1-Chloro-2-methylbutane		99.9
4-Chloro-2-methylbutane		98.8
3-Chloro-2-methylbutane		93.0
2-Chloro-2-methylbutane		86.0
Distillation range		95% between 85–109°C
Evaporation rate at 108°F:	Minutes	
	1.30	25%
	1.67	50%
	4.30	75%
	6.58	100%
Flash point (Open Cup)		34°F
Kauri-Butanol value		71 cc
Specific gravity at 20°C		0.88
Solubility in water		Negligible
Vapor pressure at 20°C		42.8 mm
Weight per gallon		7.33 lbs
Water azeotrope at 77–82°C		90% C_5H_{11} Cl (approx.)
Acidity (as HCl)		0.03% max.
Amylene and Pentane Content		3.0% max.
Color		Straw to deep purple

n-**Amyl Chloride** (1-Chloropentane) ($CH_3CH_2CH_2CH_2CH_2Cl$). Normal amyl chloride is a colorless to straw-colored liquid with a sweet odor and containing isomeric amyl chlorides and amylene as impurities. It is soluble in methyl alcohol, ethyl ether, ethyl acetate, acetone, fixed oils, mineral oil, oleic acid, hot stearic acid, aromatic and aliphatic hydrocarbons, and hot paraffin and carnauba waxes, the last two congealing when cooled.

Boiling Range	105–109°C
Distillation	95% between 104.9–108.9°C
Flash point	49°C (54°F)
Specific gravity at 20/20°C.	0.885
Solubility in water	Insoluble

Weight per gallon	7.38 lbs.
Acidity as HCl	0.025% max.
Amylene	1% max.
Color	Water-white
Other hydrocarbons	None
Polychlorides content	None

Dichloropentanes ($C_5H_{10}Cl_2$). On standing, this liquid forms hydrochloric acid, owing to the instability of some of the isomers in the mixture. The distilled product is light yellow in color and the undistilled is brown to black. It is insoluble in water but is soluble in methyl alcohol, ethyl ether, ethyl acetate, acetone, aromatic and aliphatic hydrocarbons, fixed oils, mineral oil, oleic and hot stearic acids, and hot paraffin and carnauba waxes, the latter two congealing when cooled. It dissolves oils, greases, unvulcanized rubber and some resins and bituminous substances. It is used as a metal degreasant, as an ingredient in paints and varnish removers, as a solvent in varnish and nitrocellulose lacquers, in plastics and for reclaiming rubber. It is also used as a soil fumigant. Its penetrating power is increased by mixing with lubricating oils. In combination with 20 per cent carbon tetrachloride a nonflammable mixture is formed.

Typical Properties and specifications

Distillation		95% between 130–200°C
Evaporation Rate at 109°F: Minutes		
	3.83	25%
	8.00	50%
	14.20	75%
	90.00	100%
Flash point (Open cup)		97°F
Heat of vaporization		68.5 cal./g.
Kauri-Butanol value		67 cc.
Specific gravity at 20°C		1.07–1.08
Specific heat		0.369 cal./g.
Solubility in water		Negligible
Surface tension at 25°C		31.8 dynes/cm.
Viscosity at 25°C		0.016 poise
Water content		None
Weight per gallon		8.94 lbs.
Water Azeotrope at 80–97°C		66% $C_5H_{10}Cl_2$ (approx.)
Acidity (as HCl)		0.025% max.
Average Chlorine Content		48%
Color		Light yellow

***n*-Hexyl Chloride** ($C_6H_{13}Cl$). *n*-Hexyl chloride is a water-white liquid with a sweet odor. It is soluble in methyl alcohol, ethyl ether, ethyl acetate, acetone, fixed oils, mineral oil, oleic acid, hot stearic acid, and aromatic and aliphatic hydrocarbons. It is also soluble in hot paraffin and carnauba wax; the solutions congeal on cooling. It is insoluble in water.

Boiling range	133–135°C
Flash point	95°F
Specific gravity at 20/20°C	0.877

Monochlorohydrin $[\mathrm{ClCH_2CH(OH)CH_2OH}]$ is a colorless, hygroscopic, unstable liquid made by passing hydrochloric acid gas into glycerol containing 2 per cent acetic acid. The commercial grade is a mixture of the two isomers alpha and beta, of which alpha is in the greater proportion.

Monochlorohydrin is a solvent for acetylcellulose and alkyd resins, and is able to dissolve partially ester gum, benzyl abietate, shellac, and mastic. It is miscible with water and a number of organic solvents, but will not mix with oil and hydrocarbons. A mixture of 40 per cent monochlorohydrin and 60 per cent water will dissolve cellulose acetate. It is used as an intermediate in organic synthesis.

Specific gravity	1.326 (18°C)
Boiling point	213°C
Boiling range	213–228°C (decomposes)

Dichlorohydrin $[\mathrm{ClCH_2CH(OH)CH_2Cl}$, glycerol dichlorohydrin, dichlorisopropyl alcohol, 1,3-dichlor-propanol-2, α-propenyl-dichlorhydrin] is a colorless, slightly viscous, nonflammable, unstable liquid of a faint chloroform-like odor.

In commerce it is a mixture of the two isomers 1,3-dichloro-2-hydroxypropane and 1,2-dichloro-3-hydroxypropane, of which the former predominates. It is a solvent for cellulose acetate, ethyl cellulose and some types of cellulose nitrate, benzyl abietate, soft copal, copal ester, dammar, elemi, coumarone resin, ester gum, glyptal resins, manila, mastic, shellac and so forth. The mixture of dichlorohydrins is miscible with vegetable oils and most organic solvents, and is soluble in water to the extent of 10 per cent. It is used as an intermediate in organic synthesis, as a solvent for resins and cellulose derivatives in lacquers, in celluloid cement, and as a binder for water colors.

Specific gravity	1.36–1.39
Boiling range	174°–176°C (95%)
Boiling point	(1.3)174°C–(1.2)183°C
Refractive index	1.47–1.48
Flash point	74°C
Vapor pressure	7 mm

Epichlorohydrin (Chloropropylene oxide, 1-chloro-2,3-epoxypropane) $(\underbrace{\mathrm{O \cdot CH_2 \cdot CH}} \cdot \mathrm{CH_2Cl})$. Epichlorohydrin is a water-white, highly volatile, reactive liquid with a characteristic odor. It is miscible with lower aliphatic alcohols, ethers, esters, ketones, aliphatic, halogenated hydrocarbons, fixed oils, carbon tetrachloride, benzene, gasoline, and aliphatic halogen derivatives. It is immiscible with water, glycerin, and petroleum hydrocarbons. It is a powerful solvent for many types of cellulose esters and ethers, synthetic and natural resins and gums. It is a solvent for ester gum, rosin, and cellulose acetate, and when mixed with butyl acetate it becomes compatible with cellulose nitrate. It is used principally as a raw material for the synthesis of pharmaceuticals, resins etc.

Boiling point	116.11°C (760 mm)
Boiling range (A.S.T.M. gasoline still) at 736 mm	90% between 114–118°C
Specific gravity at 25/25°C	1.1839
Refractive index at 25°C	1.439
Freezing point	−57.2°C
Vapor pressure at 20°C	13.0 mm
Flash point (Tag open cup)	105°F
Weight per gallon	9.83 lbs.

Propylene Chlorohydrin (Chloro-isopropyl alcohol) ($CH_3 \cdot CHOH \cdot CH_2Cl$). Propylene chlorohydrin is a colorless liquid with a mild odor and freely soluble in water. It is principally used in organic synthesis for the introduction of the hydroxypropyl group.

Acidity (as HCl)	0.02% by wt.
Boiling point (760 mm)	127.5°C
Color	Water-white
Specific gravity at 20/20°C	1.1270
Solubility in water	Miscible in all proportions
Weight per gallon at 20°C	9.3 lbs.
Constant-boiling mixture at 760 mm: Chlorohydrin approx. 46% + Water 54%	B.P. 95.4°C

Glycerol Alpha-Monochlorohydrin ($ClCH_2CHOHCH_2OH$). Glycerol α-monochlorohydrin is a water-white to light brown viscous liquid with very little odor. It is soluble in water, ethyl and methyl alcohols, glycerol, ethyl ether, ethyl acetate, acetone, fixed oils, and oleic acid. It is insoluble, however, in benzene, gasoline, carbon tetrachloride, aromatic and aliphatic hydrocarbons, mineral oil, ester gum, dammar gum, carnauba wax, paraffin wax, rosin, and linseed oil. It is a solvent for cellulose acetate and nitrocellulose when mixed with a butyl acetate solution. Its solvent properties are due to the hydroxyl and chloride groups in the molecule. It is used principally in organic synthesis.

Boiling point	213°C
Boiling range (A.S.T.M.)	90% between 136–142°C at 40 mm
Flash point (open cup)	280°F
Specific gravity at 20/4°C	1.320
Refractive index at 25°C	1.4781
Solubility in water	100%
Weight per gallon	10.98 lbs.

Glycerol Alpha, Gamma Dichlorohydrin (Dichlorohydrin, dichloroisopropyl alcohol, 1,3-Dichloro-propanol-2, propenyl dichlorohydrin) ($ClCH_2—CHOH—CH_2Cl$). Glycerol α,γ-dichlorohydrin is a colorless to light brown, slightly viscous, nonflammable and unstable liquid with a faint chloroform-like odor. The commercial solvent is a mixture of the two isomers 1,3-dichloro-2-hydroxypropane and 1,2-dichloro-3-hydroxypropane, the former being in larger proportion. It is soluble in methyl and ethyl alcohols, glycerol, ethyl ether, acetone, fixed oils, oleic acid, aromatic hydrocarbons, carbon tetrachloride, and most organic solvents, but only slightly soluble in water and gasoline. It is insoluble in aliphatic hydrocarbons, mineral oil, paraffin wax and carnauba wax. It is a solvent for cellulose acetate, ethyl cellulose, some types of cellulose nitrate, benzyl abietate, soft copal, copal ester, elemi, coumarone resin, ester gum, glyptal resins, manila, mastic, shellac, linseed oil, rosin, etc. However, it will not dissolve dammar gum or carnauba wax. It is used as an intermediate in organic synthesis.

It has been suggested as a poison for rodents. About 80 solvent mixtures have been proposed as solvents for ethyl cellulose in which dichlorohydrin plays an important part. These mixtures are miscible with vegetable oils and most organic solvents and are soluble in 10 per cent of water.

Boiling point	172–178°C
Boiling range (A.S.T.M.)	90% between 172–178°C (136 mm)
Flash point	74°C
Specific gravity at 25/25°C	1.3591
Refractive index at 25°C	1.479
Vapor pressure	7 mm
Weight per gallon	11.33 lbs.

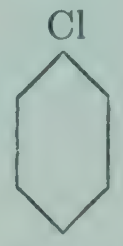
AROMATIC

Monobromobenzene (C_6H_5Br, phenyl bromide, bromobenzene). Monobromobenzene is a heavy, mobile, colorless liquid of pleasant characteristic odor. It is an efficient solvent for many substances and is miscible with both petroleum products and halogenated solvents. Bromobenzene is used as an intermediate in organic synthesis. It is added to motor fuels both for its ability to dissolve and remove "gasoline gum" and for the lubricating properties it imparts. It is also used as a crystallizing solvent for organic substances.

Molecular weight	156.96
Boiling point	156.6° C 312.9° F
Freezing point	−30.5° C −22.9° F
Flash point	65° C
Specific gravity	1.499 (15° C)
Weight per gallon	12.51 lbs.

Dibromobenzene ($C_6H_4Br_2$, *o*-dibromobenzene). Dibromobenzene is a heavy liquid of pleasant aromatic odor. It is completely miscible with most solvents and is a particularly good solvent for oils. It is added to gasolines for its ability to dissolve gummy and waxy deposits. Other uses are in organic synthesis and in the separation of ores by flotation.

Monochlorobenzene (Chlorobenzene, phenyl chloride, Monochlorobenzol)



Monochlorobenzene is a colorless, mobile, volatile and flammable liquid with an almond-like odor. It is considered less toxic than benzene. This solvent is made by the chlorination of benzene in the presence of a chlorine-carrier. It is insoluble in water but soluble in ethyl alcohol, ethyl ether, carbon tetrachloride and most organic solvents. It will dissolve ethyl

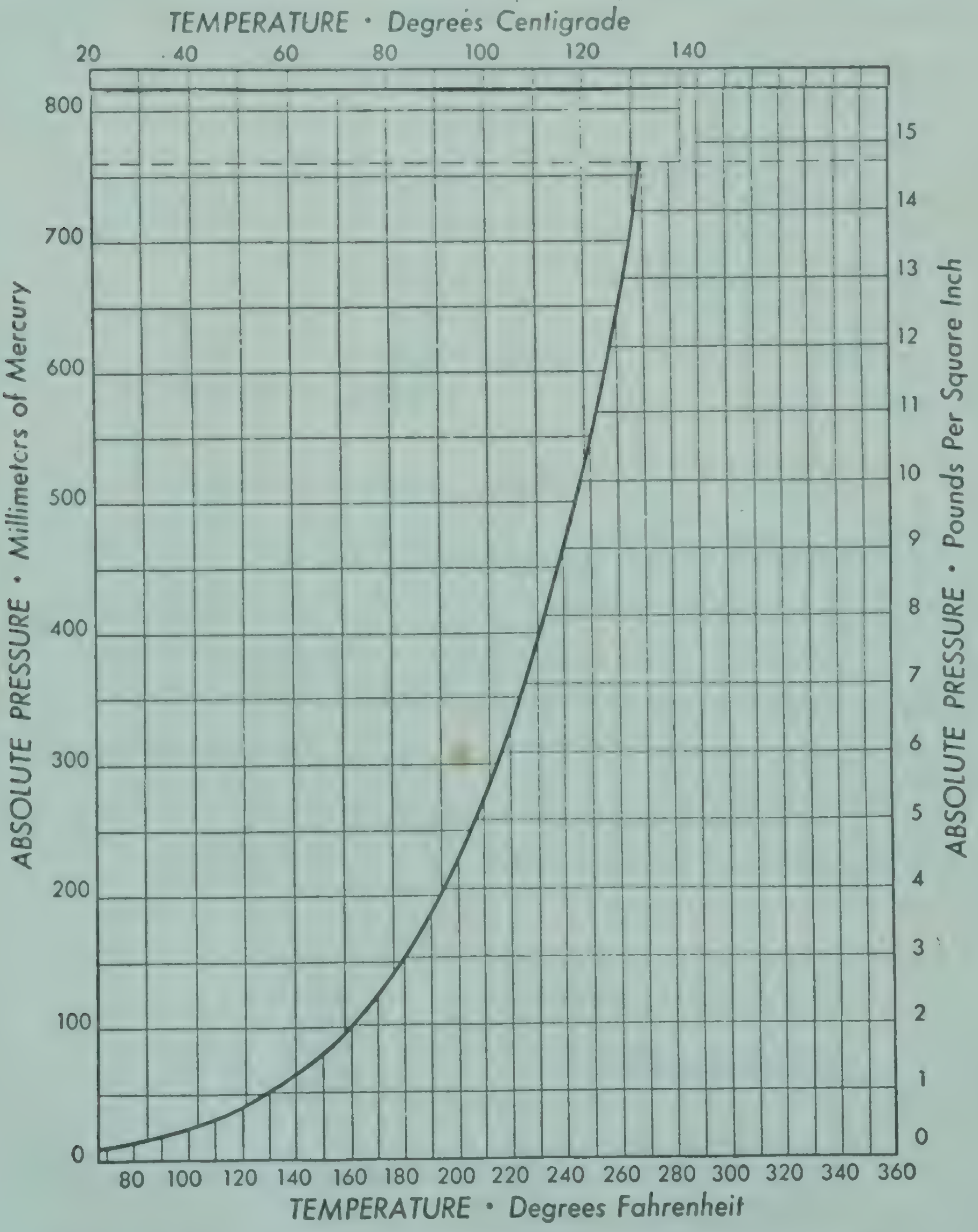


Figure 8.27. Vapor Pressures of Monochlorbenzene.[6]

cellulose, many natural and synthetic resins, such as rosin, dammar, soft copal, vinyl resins, "Bakelite," acetylcellulose, etc. In common with other halogenated hydrocarbons, the solvent power of chlorobenzene is increased by adding amyl, butyl, ethyl or methyl alcohol or their acetate esters. It is added to lacquers for its unique property of producing a crackle or matt effect. It is used in the manufacture of chemicals, such as aniline, phenol and picric acid, poison gases, dyes, drugs, synthetic perfumes, and insecticides. It is a solvent for removing paint, tars, etc., and is used in organic synthesis.

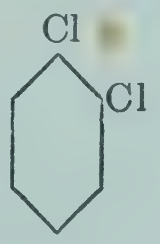
Typical Properties and Specifications

Boiling point (760 mm)	131.6°C
Dielectric constant, 1000 cycle	5.53
Electrical conductivity at 0°C	10^{-9} recip. ohm
Fire point	36°C
Flash point	27°C
Freezing point	−45°C
Latent Heat of vaporization at B.P.	77.6 cal./g.
Specific gravity at 15/4°C	1.1117
Specific heat	0.30 cal./g./°C
Specific resistivity	7.8 x 10^9 ohms/cm.
Refractive index at 15°C	1.527.48
Solubility in water at 30°C	0.049% by wt
Surface tension (C.G.S. units)	33.08
Vapor pressure at 20°C	8.71 mm
Viscosity at 15°C	0.00844 cgs unit
Weight per gallon at 25°C	9.19 lbs.

Azeotropic Mixture

Monochlorobenzene	72%
Acetic acid	28%
Boiling point	114.65°C

o-**Dichlorobenzene** (1,2-Dichlorobenzene, orthene)



o-Dichlorobenzene is a heavy, colorless, volatile, and stable liquid, with an aromatic odor. It is considered nonflammable, but will burn when ignited. This solvent is a mixture composed principally of *ortho* compounds and containing varying amounts of *para* and *meta* isomers. It is insoluble in water but soluble in ethyl alcohol, ethyl ether, benzene, carbon tetrachloride and most common solvents. It is a solvent for oxides of nonferrous

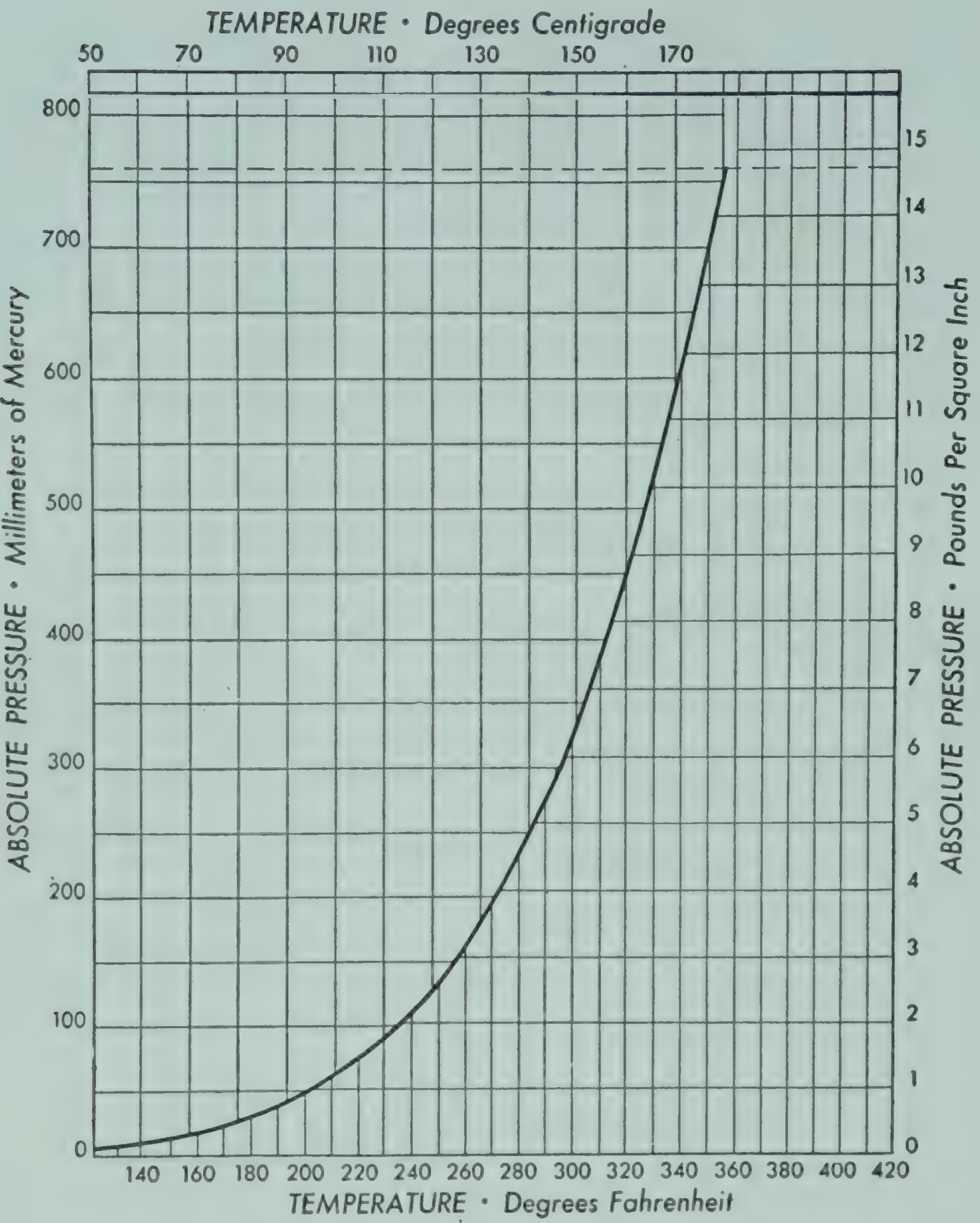


Figure 8.28. Vapor Pressures of Orthodichlorbenzene.[6]

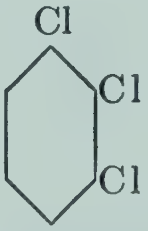
metal, waxes, tars, unvulcanized rubber, greases, oils, asphalts, sulfur, organic sulfur derivatives, natural and synthetic gums and resins, acetylcellulose, etc.

It is added to lacquers and varnishes for its solvency, penetration, slow evaporation and its ability to impart easy working equalities and freedom from orange peel. It is used for degreasing metals, leather, hides, automobiles, and as an ingredient in metal polish. It is a wax solvent, an anti-skinning agent in varnishes, a termite exterminator, repellent and wood preservative and has use as a fungicide, preservative and fumigant. It is employed as a spotting agent, tar solvent, and in the organic synthesis of dyes and drugs. It is also used in the removal of sulfur from illuminating gases.

Typical Properties and Specifications

	Purified	*Technical*
Boiling point	180.2°C	179.6°C
Dielectric constant (1000 cycles)	9.82	
Electrical conductivity at 0°C	10^{-9} recip. ohm	
Fire point	103°C	103°C
Flash point	68°C	68°C
Freezing point	−18.3°C	−22.5°C
Heat of combustion	671.8 kg. cal./mol.	
Heat of fusion	88 joules/g.	
Latent heat of vaporization		65 cal./g. at B.P.
Specific gravity at 20/4°C		1.3048
Specific heat		0.271 cal./g./°C
Specific resistivity		2.0 x 10^8 ohms/cm.
Refractive index at 22°C		1.5518
Solubility in water at 25°C		Less than 0.01%
Weight per gallon at 25°C		10.85 lbs.
Boiling range, within	30°C	4.0°C
Impurities, (*p*-dichlorobenzene trichlorobenzene)	Not over 4%	Not over 12%

Trichlorobenzene



Trichlorobenzene is a mixture of 1,2,3- and 1,2,4-trichlorobenzenes with an odor much like *o*-dichlorobenzene. It is insoluble in water, partially soluble in ethyl alcohol, and soluble in ethyl ether, benzene, carbon tetrachloride, and most organic solvents. It is a solvent for fats, oils, waxes, and resins. It is used in the manufacture of oil-soluble dyes and intermediates, as a dielectric fluid, as an addition agent to some lubricating oils, as a solvent for degreasing metals, as a crystallizing medium, in insecticide compositions and for termite extermination.

Typical Properties and Specifications

Boiling point	214.8°C
Dielectric constant, 1000 cycles	4.93
Dielectric strength (0.1″ gap)	30,000 volts
Fire point	Above 213°C
Flash point	103°C
Freezing point	7.5°C
Latent heat of vaporization	58.2 cal./g. at B.P.
Pour point	Below 10°C
Specific gravity 25/25°C	1.460
Specific heat	0.20 cal./g./°C

Specific resistivity	2.9 x 10^9 ohms/cm
Refractive index 20°C	1.5671
Weight per gallon 25°C	12.15 lb.
Boiling range	Within 3°C
Color	Colorless
Impurities,	Not over 12% 1,2,3-trichlorobenzene
Purity	Contains over 99% $C_6H_3Cl_3$

o-**Chlorotoluene** $[\underline{CH{=}CH{-}CH{=}CH{-}C(CH_3){=}CCl}]$. *o*-Chlorotoluene is a colorless liquid with a characteristic odor. It is insoluble in water but freely soluble in ethyl ether. It is a solvent for rubber and synthetic resins, and is used in the manufacture of rubber accelerators and in organic synthesis.

Freezing point (approx.)		−36°C
Water		Nil
Specific gravity at 25/15°C		1.078–1.079
Refractive index at 22°C		1.5231
Surface tension at 25°C		35.11 dynes/cm.
Purity (minimum)		99.0%
Boiling range (typical)	Initial	159.0°C
	50%	159.4 C
	Dry	160.0 C

p-**Chlorotoluene** $[\underline{CH{=}CH{-}C(CH_3){=}CH{-}CH{=}CCl}]$. *p*-Chlorotoluene is a colorless liquid with a characteristic odor. It is insoluble in water but freely soluble in ethyl ether. It is a solvent for rubber and synthetic resins. It is used in organic synthesis and in the manufacture of rubber accelerators.

Freezing point (approx.)		6.5°C
Water		Nil
Specific gravity at 25/15°C		1.065–1.067
Refractive index at 22°C		1.5184
Surface tension at 25°C		34.60 dynes/cm.
Purity (minimum)		97.0%
Boiling range (typical)	Initial	162.0 C
	50%	162.4 C
	Dry	166.0 C

Monochlorotoluene ($CH_3C_6H_4Cl$). The technical grade of this solvent is a mixture of the *ortho* and *para* derivatives. It is a clear, colorless, liquid with an odor resembling monochlorobenzene and is insoluble in water but freely soluble in ethyl ether. It is a solvent for rubber and synthetic resins and is used in the manufacture of rubber accelerators as well as in organic synthesis.

	Ortho	*Para*
Boiling point	159.4°C	162.5°C
Distillation range, Start	158.3°C min.	
100%	165.1°C max.	
Flash point	46°C	
Freezing point	34°C	7.5°C
Purity	60% approx.	40% approx.
Specific gravity at 20/4°C	1.0817	1.0697
Refractive index at 20°C	1.5238	1.5199
Weight per gallon at 25°C	9.1 lbs.	

α-Chloronaphthalene ($C_{10}H_7Cl$). This solvent is a clear, colorless liquid with a persistent characteristic odor. It is soluble in alcohol, and ether, but insoluble in water. It is used as a heat-transfer medium, valve lubricant in internal combustion engines, in compositions for removing carbon from cylinders of internal combustion engines, and in organic synthesis.

Boiling point (at 760 mm)	263°C
Fire point	170°C
Flash point	95°C
Freezing point	−13.4°C
Specific gravity at 20/4°C	1.194
Refractive index at 20°C	1.6332
Surface tension	41.80 cgs units
Vapor pressure at 60°C	0.39 mm
Weight per gallon at 25°C	10 lbs.

Monoamyl chloronaphthalene ($C_5H_{11}C_{10}H_6Cl$). This solvent is a straw-colored liquid with a naphthalene-like odor. It is soluble in ethyl ether, ethyl acetate, acetone, fixed oils, mineral oil, oleic acid, and aromatic and aliphatic hydrocarbons. It is also soluble in hot paraffin wax, carnauba wax and stearic acid but these congeal on cooling. It is insoluble in water and methyl alcohol.

Flash point	295°F
Specific gravity at 20/20°C	1.076

Diamyl chloronaphthalene [$(C_5H_{11})_2C_{10}H_5Cl$]. This solvent is an orange-colored liquid with a naphthalene-like odor. It is soluble in ethyl ether, ethyl acetate, acetone, fixed oils, mineral oil, oleic acid, and aromatic and aliphatic hydrocarbons. It is also soluble in hot paraffin wax, carnauba wax, and stearic acid, but these congeal on cooling. It is insoluble in water and methyl alcohol.

Boiling range (760 mm)	352–377°C
Flash point	330°F
Specific gravity at 20/20°C	1.06

Dichloroethyl Ether (2,2′-Dichloroethyl ether, *sym.* or β,β′-Dichloroethyl ether) ($ClCH_2CH_2OCH_2CH_2Cl$). Dichloroethyl ether is a colorless, stable, and noncorrosive liquid with an odor much like ethylene dichloride. It is insoluble in hydrocarbons but soluble in most organic solvents. It is an active solvent for oils, fats, waxes, gums, tars, natural and synthetic resins, soaps and ethyl cellulose. When mixed with an alcohol, it dissolves many types of cellulose esters and ethers, as a result of the combined action of the ethyl ether and ethylene dichloride groups in the molecule.

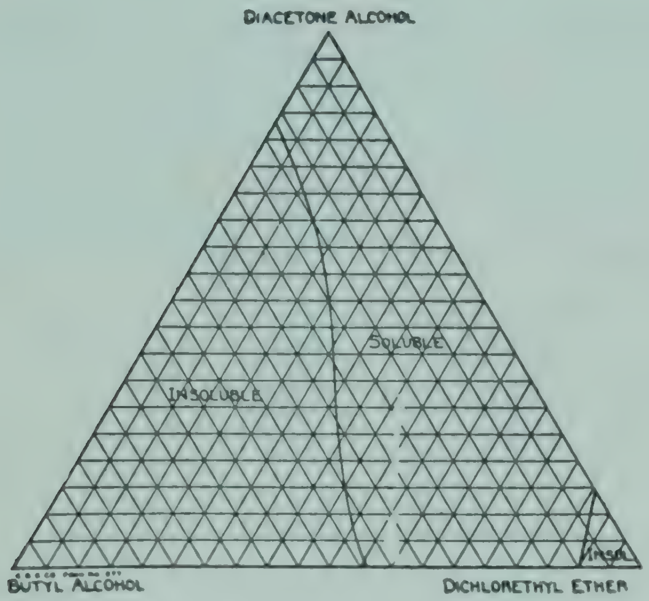


Figure 8-29. Solubility of Low Viscosity Cellulose Acetate in Mixtures of Diacetone Alcohol, Butyl Alcohol and Dichloroethyl Ether.[7]

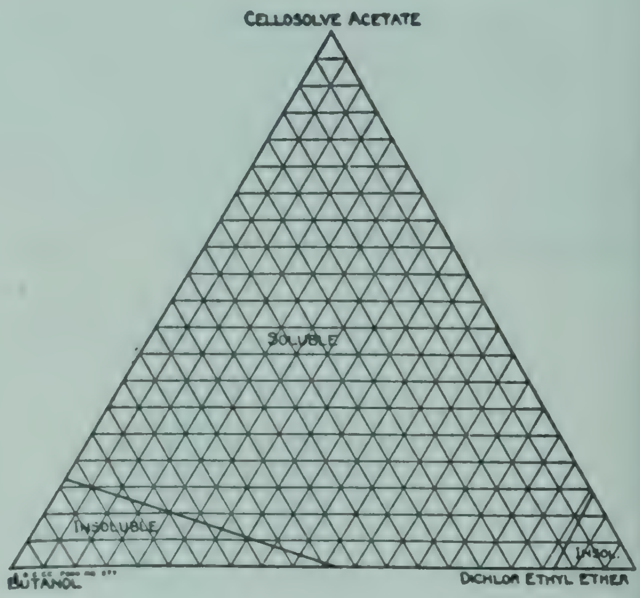


Figure 8-30. Solubility of ½ Second R. S. Nitrocellulose in Mixtures of Cellosolve Acetate, Butanol and Dichloroethyl Ether.[7]

In general, this solvent can replace ethylene dichloride, particularly in processes where high temperatures are required. It is used in paint and varnish removers, in spotting agents, and cleaning solutions. Because of its detergent action it can assist soap solutions in such textile processes as kier boiling, and scouring for the removal of paint, tar, oil, and grease spots. It is used in the textile industry as a softening and conditioning agent, as a substitute for caustic alkalies in kier boiling, in peroxide bleaching for penetration, in desizing and as an aid in mercerizing. It is also employed as a selective solvent in the manufacture of high-grade lubricating oils from crude oils.

Typical Properties and Specifications

Boiling point	178°C
Flash point (closed cup)	55°C
Apparent Ignition Temperature in Air	396°C
Latent heat of vaporization at 178°C	64.1 cal./g.
Specific gravity at 20/20°C	1.219 to 1.224
Specific heat at 20–30°C	0.369 cal.

Refractive index at 20°C	1.457
Surface tension at 25°C	41.8 dynes/sq. cm.
Viscosity at 25°C	2.0653 centipoises
Vapor pressure at 20°C	1.2 mm
Weight per gallon at 20°C	10.17 lbs.
Acidity (as HCl)	0.005% max.
Boiling range (760 mm.)	Not more than 5% distills below 173°C Not less than 95% distills below 179°C
Color (500 mm. tube)	Not more than 2 yellow Lovibond
Ethylene dichloride	1.0% max.

Dichlorodiisopropyl Ether [$ClCH_2CH(CH_3)—O—CH(CH_3)CH_2Cl$]. This compound is a colorless liquid with a mild odor; its properties are very much like those of dichloroethyl ether. It is miscible with practically all oils as well as most organic solvents. It is a good solvent for fats, waxes, greases, and hydrocarbons, and is used as a high-boiling solvent, as an extractant, and in organic synthesis. It may also be used as a spotting agent, in cleaning solutions, and in paint and varnish removers.

Typical Properties and Specifications

Boiling point (760 mm)	187.3°C
Flash point (open cup)	185°F
Specific gravity at 20/20°C	1.1122
Solubility in water at 20°C	0.17% by wt.
Solubility of water in solvent at 20°C	0.11% by wt.
Vapor pressure at 20°C	0.85 mm.
Weight per gallon at 20°C	9.26 lbs.
Acidity (as HCl)	0.01% by wt. max.
Boiling range (760 mm)	Not more than 5% distills below 180°C Not less than 95% distills below 190°C
Color (Pt-Co scale)	25 max.

Trigylcol Dichloride [$Cl(CH_2CH_2O)_2CH_2CH_2Cl$]. This solvent is a colorless liquid with a mild odor. It is miscible with practically all oils as well as with most organic solvents. It is a good solvent for fats, waxes, greases, and hydrocarbons, and is used as a high-boiling solvent, as an extractant, and in organic synthesis. It may also be used as a spotting agent, in cleaning solutions, and in paint and varnish removers.

Typical Properties and Specifications

Boiling point (760 mm)	241.3°C
Flash point (open cup)	250°F
Specific gravity at 20/20°C	1.1950 to 1.2000
Solubility in water at 20°C	1.89% by wt.
Solubility of water in solvent at 20°C	0.83% by wt.
Vapor pressure at 20°C	0.06 mm
Weight per gallon at 20°C	9.97 lbs.
Acidity (as HCl)	0.01% by wt. max.
Boiling range (760 mm)	Not more than 5% distills below 235°C Not less than 95% distills below 242°C
Color (Pt-Co scale)	25 max.
Dryness at 20°C	Miscible with 19 vol. 60° Be gasoline

Halowax Oils. Halowax oils are thin, neutral, mobile, almost colorless liquids of a characteristic heavy odor. They are insoluble in alkaline solutions but are soluble in carbon tetrachloride, benzene, and most organic solvents and oils. They dissolve many types of dyes, gutta percha, unvulcanized rubber, mineral and vegetable oils, resins, varnish gums and waxes. Halowax oils are non-corrosive to metals and are high in dielectric strength.

Liquid at	−31°C
Freezing point	−36°C
Flash point	111°C
Boiling range	(about) 250–288°C
Specific heat	0.282 (between 30–60°C)
Specific gravity	1.20–1.27 (20°C)

FLUORINATED HYDROCARBONS

The fluorochloromethanes were originally proposed[10] in 1930 as having chemical and physical properties making them particularly suitable for use as refrigerants. As a result, dichlorodifluoromethane and its homologs were developed to commercial proportions as refrigerants, under the trademark "Freon".[4] Other members of this group have been studied by Benning and McHarness[11] for the purpose of determining their possibilities as refrigerants. The "Freon" flourinated solvents are distinguished by their relative stability toward metals of construction, and by their low order of toxicity and nonflammability.

Dichlorodifluoromethane ("Freon-12") (CCl_2F_2).

This water-insoluble compound is a gas miscible with many solvents. In the field of insecticidal sprays[2] new advances have been made by utilizing low-boiling solvents as a means of dispersing insecticides. Some of the more promising solvents that will give a fine dry spray and, at the same time, be free from fire hazard and toxicity, are dichlorodifluoromethane, methyl chloride, and a mixture of propane and dichlorodifluoromethane.

Boiling point	−29.8°C
Specific gravity at −30°C	1.486
Critical temperature	198.0°C
Critical pressure	43.2 atm
Critical density	0.554
Freezing point	−111°C

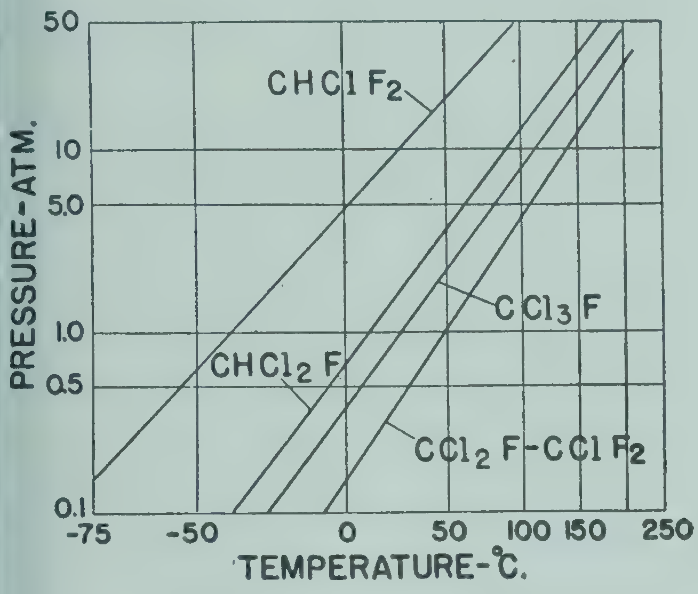


Figure 8-31. Vapor Pressure of Fluorochloro Hydrocarbons.[4]

Difluorochloromethane ("Freon-22") ($CHClF_2$).

Typical Properties and Specifications

Boiling point (760 mm.)	−40.8°C
Critical temperature	96.0°C
Critical pressure	48.7 atm
Critical density	0.523 g./cc.
Freezing point	−160°C
Color	Clear and water white
Odor	Ethereal and similar to carbon tetrachloride (Odorless when mixed with air)
Moisture	.005% by wt., max.
Non-condensible gases	5.0% by vol., max., in vapor phase
High-boiling impurities	0.05% by vol., max.
Chlorides	None

Fluorodichloromethane ("Freon-21") ($CHCl_2F$). Fluorodichloromethane is a gas at ordinary temperatures; it is soluble in alcohol and ether but insoluble in water.

Typical Properties and Specifications

Boiling point	8.9°C
Critical pressure	51.0 atm
Critical temperature	178.5°C
Critical density	0.522 g./cc.
Freezing point	−135°C
Specific gravity at 0°C	1.426
Color	Clear and water-white
Odor	Ethereal and similar to carbon tetrachloride (Odorless when mixed with air)
Moisture	0.005% by wt., max.
High-boiling impurities	0.05% by vol., max.
Chlorides	None

Fluorotrichloromethane ("Freon-11") (CCl_3F). Fluorotrichloromethane is a colorless liquid.

Typical Properties and Specifications

Boiling point	23.7°C
Critical density	0.554 g./cc.
Critical pressure	43.2 atm
Critical temperature	198.0°C
Freezing point	−111°C
Specific gravity at 17.2°C	1.494
Color	Clear and water-white
Odor	Ethereal and similar to carbon tetrachloride (Odorless when mixed with air)
Moisture	0.0025% by wt., max.
High-boiling impurities	0.05% by vol., max.
Chlorides	None

Trifluorotrichloroethane ("Freon-113") ($CCl_2F—CClF_2$).

Typical Properties and Specifications

Boiling point	47.6°C
Critical temperature	214.1°C
Critical pressure	33.7 atm
Critical density	0.576 g./cc.
Freezing point	−35°C
Color	Clear and water white
Odor	Ethereal and similar to carbon tetrachloride
Moisture	0.002% by wt. max.
High-boiling impurities	0.03% by vol. max.
Chlorides	None

Table 8.17. Viscosities of "Freon" Solvents[12]

	VAPOR					LIQUID				
	5°F	20°	40° Centi-poises	100°	150°	5°F.	20°	40° Centi-poises	80°	100°
Ammonia	.0085	.0088	.0093	.0105	.0116	2.50	.240	.230	.210	.200
"Freon-113"	.0093	.0095	.0098	.0106	.0112	1.20	1.043	.876	.646	.564
Methyl chloride	.0095	.0098	.0102	.0112	.0120	.290	.280	.260	.230	.220
"Freon-11"	.0096	.0099	.0103	.0113	.0121	.650	.586	.517	.417	.380
"Freon-21"	.0102	.0105	.0108	.0118	.0125	.470	.436	.397	.337	.314
Sulfur dioxide	.0111	.0115	.0120	.0134	.0144	.503	.390	.350	.290	.260
"Freon-12"	.0114	.0116	.0119	.0129	.0136	.328	.308	.286	.255	.242
Carbon dioxide	.0132	.0135	.0140	.0155	.0165	.115	.110	.095	.064	—
Water	—	—	—	—	—	—	—	1.54	.86	68

Table 8.18. Explosive Properties of "Freon" Solvents[12]

REFRIGERANT	EXPLOSIVE RANGE CONCENTRATION IN AIR		MAXIMUM EXPLOSION PRESSURE, LB./SQ. IN. GAGE	TIME OF DEVELOPMENT OF PRESSURE, SECONDS
	% by vol.	lb./1000 cu. ft.		
Ammonia	16 to 25	7.1 to 11.05	50	0.175
Methyl formate	4.5 to 20.0	7.02 to 31.2	96	0.026
Methyl chloride	8.1 to 17.2	10.6 to 22.6	69	0.110
Dichlorethylene	5.6 to 11.4	14.1 to 28.7	76	0.095
Ethyl chloride	3.7 to 12.0	6.21 to 20.1	87	0.028
Sulfur dioxide		Non-flammable		
Methylene chloride		"		
"Freon-21"		"		
"Freon-113"		"		
"Freon-11"		"		
"Freon-114"		"		
"Freon-12"		"		

Table 8.19. Freezing Points of "Freon" Solvents[12]

"Freon-12"	−252.4°F
Isobutane	−229.0
"Freon-21"	−211.0
Methyl formate	−148.0
Methyl chloride	−143.68
Methylene chloride	−143.0
"Freon-11"	−168.0
Ammonia	−107.86
Sulfur dioxide	−98.86
Carbon dioxide	−69.9 triple
"Freon-113"	−31.0

TABLE 8.20. TOXIC PROPERTIES OF "FREON" SOLVENTS[12]

UNDERWRITERS' LABORATORY GROUP NO.	REFRIGERANT	FORMULA	CUBIC FEET PER LB. OF REFRIGERANT, 68°F 1 ATMOS.	BOILING POINT, °F	KILLS OR SERIOUSLY INJURES		
					Duration of exposure	Concentration in air	
						% by vol.	Lb./1000 cu. ft.
1	Sulfur dioxide	SO_2	6.01	14.0	5 min.	.7	1.165
2	Ammonia	NH_3	22.6	−28.0	½ hour	.5 to .6	.221 to .256
3	Methyl formate	$C_2H_4O_2$	6.41	89.2	1 hour	2 to 2.5	3.12 to 3.9
4	Methyl chloride	CH_3Cl	7.62	−10.6	2 hours	2 to 2.5	2.62 to 3.28
4	Dichlorethylene	$C_2H_2Cl_2$	3.97	118	2 hours	2 to 2.5	5.04 to 6.3
a4	Ethyl chloride	C_2H_5Cl	5.96	54.5	1 hour	4.0	6.72
a4	Methylene chloride	CH_2Cl_2	4.53	103.6	½ hour	5.1 to 5.3	11.25 to 11.70
b4	"Freon-113"	$C_2Cl_3F_3$	2.1	117.6	—	—	—
b4	"Freon-21"	$CHCl_2F$	3.76	48.0	½ hour	10.2	27.1
5	Carbon dioxide	CO_2	8.75	−108.4	½ to 1 hour	29.0 to 30.0	33.2 to 34.3
5	"Freon-11"	CCl_3F	2.8	74.7	2 hours	10	35.7
6	"Freon-114"	$C_2Cl_2F_4$	2.25	38.4	2 hours	*20.1 to 21.5	89.6 to 95.7
6	"Freon-12"	CCl_2F_2	3.18	−21.7	2 hours	*28.5 to 30.4	89.6 to 95.7

* Oxygen deficiency.

Dichlorotetrafluoroethane ("Freon-114") ($CClF_2$—$CClF_2$).

Typical Properties and Specifications

Boiling point (760 mm)	38.4°F (3.55°C)
Melting point	−137°F (−94°C)
Critical temperature	294.3°F (145.7°C)
Critical pressure	474 lbs./sq. in. abs.

Specific Heat of Vapor
(1 atm.)

Temp. °F.	c_p	c_v	c_p/c_v
110	.1629	.1502	1.085
160	.1696	.1571	1.080
210	.1763	.1641	1.074

Temp.	Viscosity (centipoise) Vapor (1 atm.)	Liquid (Sat'n. pressure)
−40	0.0095	.879
−20	.0098	.711
0	.0102	.598
20	.0106	.516
40	.0109	.454
60	.0112	.405
80	.0116	.366
100	.0119	.334
120	.0122	.307
140	.0125	.284

Color	Clear and water white
Odor	Faint and ethereal
Moisture	Not more than .0025% by weight
Non-condensible gases	Not more than 5.0% by volume in vapor phase
High-boiling impurities	Not more than 0.05% by volume
Chlorides	None
Toxicity	Group 6 Classification of Underwriters' Laboratories Report MH-2375
Flammability	Noncombustible and nonflammable (Underwriters' Laboratories Report MH-2375)

"Genetron 101" ($CH_3 \cdot CClF_2$).

Typical Properties and Specifications

Physical state	Colorless liquefied gas
Boiling point	−9.2° C (15.4°F)
Melting point	−130.8° C (−203.4° F)
Latent heat of vaporization at B. P.	53.25 cal./g.
Specific gravity at B. P.	1.194
Specific heat at B. P.	0.293

Vapor pressure:

Temperature °F	*Vapor Pressure (p.s.i.a.)*
70	44.9
100	74.5
130	114.5

TABLE 8.21. SOLUBILITY OF "FREON-12" AT 21.1°C. AND ATMOSPHERIC PRESSURE[4]

SOLVENT	I.P./100	WT. % "FREON-12"	MOL. FRACTION "FREON-12"
Dibutyl ether	25	14.1	0.15
Dibutyl tartrate	25	6.2	.12
Butyl butyrate	27	13.2	.14
Dibutyl oxalate	27	8.9	.13
Isoamyl benzoate	30	8.6	.13
Amyl chloride	31	13.1	.12
Diethyl phthalate	31	4.7	.082
Diethyl aniline	32	7.2	.093
Xylene	34	11.3	.095
Carbon tetrachloride	34	5.2	.063
Toluene	35	11.6	.091
Ethylene glycol butyl ether	35	7.2	.070
Dichlorethyl ether	35	3.9	.046
Diacetone Alcohol	36	6.1	.060
Phenetole	36	7.4	.070
Benzene	38	9.0	.060
Dioxan	39	6.9	.054
Chloroform	39	5.5	.052
n-Butyl alcohol	40	8.5	.054
Brombenzene	40	5.0	.063
Methyl salicylate	41	3.0	.040
Ethylene glycol ethyl ether	42	7.4	.055
Cyclohexanone	42	8.5	.069
α-Chloronaphthalene	42	3.9	.052
Ethylene dichloride	43	4.7	.039
Bromoform	45	1.2	.025
Nitrobenzene	46	4.1	.039
Methyl Alcohol	78	5.7	.015
Water (Temp. 26°C.)	200	.028	

(One vol. of H_2O dissolves. .057 vol of 'Freon-12" vapor).
SOURCE: Kinetic Chemicals, Inc. (Division of DuPont).

Solubility:

	Weight % CH_3CClF_2	
Solvent	*0°C*	*27.5° C*
Water	0.30	0.15
20% NaOH solution	0.17	0.09
25% NaCl solution	0.20	0.07
34.5% HCl solution	0.24	0.12

"Genetron 100" ($CH_3 \cdot CHF_2$).

Typical Properties and Specifications

Physical state	Colorless liquefied gas
Boiling point	−24.7° C (−12.5° F)
Melting point	−117° C (−178.6° F)
Critical temperature	107.5° C (225.5° F)

(*Continued on page 3*

TABLE 8.22. SOLVENT ACTION OF FLUORINE-SUBSTITUTED CHLORETHYLENES[13]

SOLUTE	$C_2Cl_3F_3$	$C_2Cl_4F_2$
Inorganic Compounds		
Ammonium nitrate	Insol.	Insol.
Ammonium fluosilicate	Insol.	Insol.
Ammonium thiocyanate	Insol.	Insol.
Asbestos	Insol.	Insol.
Barium dioxide	Insol.	Insol.
Boric acid	Insol.	Insol.
Cadmium iodide	Insol.	Insol.
Chromium oxalate	Insol.	Insol.
Chromium chloride (violet)	Insol.	Insol.
Iodine	Insol.	Slightly sol.
Potassium antimonyl tartrate	Slightly sol	Insol.
Potassium chromate	Insol.	Insol.
Potassium permanganate	Insol.	Insol.
Silver nitrate	Insol.	Insol.
Sodium carbonate	Insol.	Insol.
Water	Insol.	Insol.
Organic Acids and Acid Anhydrides		
Anthranilic acid	Very slightly sol.	Insol.
Benzoic acid	Moderately sol.	Very sol.
Malic acid	Very slightly sol.	Insol.
Malonic acid	Insol.	Insol.
Mandelic acid	Insol.	Insol.
Monochloroacetic acid	Insol.	Insol.
Phthalic anhydride	Moderately sol.	Moderately sol.
Salicylic acid	Very slightly sol.	Moderately sol.
Stearic acid	Moderately sol.	Slightly sol.
Succinic acid	Very slightly sol.	Very slightly sol.
Tartaric acid	Very slightly sol.	Very slightly sol.
Resins, Gums, Fats, Oils, etc.		
Amberol F7 light	Slightly sol.	Slightly sol.
Bakelite XR821	Insol.	Insol.
Dammar	Moderately sol.	Very sol.
Ester gum	Moderately sol.	Insol.
Glyptal 1102	Insol.	Insol.
Shellac	Insol.	Insol.
Agar	Insol.	Insol.
Gelatin	Very slightly sol.	Very slightly sol.
Gum arabic	Insol.	Insol.
Gum mastic	Slightly sol.	Insol.
Casein	Insol.	Insol.
Egg albumen	Insol.	Insol.
Coca butter	Very sol.	Soluble
Castor oil	Very sol.	Miscible
Cottonseed	Very sol.	Miscible

TABLE 8.22. SOLVENT ACTION OF FLUORINE-SUBSTITUTED CHLORETHYLENES[13] (*Continued*)

SOLUTE	$C_2Cl_3F_3$	$C_2Cl_4F_2$
Aliphatic Solutes		
n-Hexane	Miscible	Miscible
n-Heptane	Miscible	Miscible
Kerosene	Miscible	Miscible
Carbon tetrachloride	Miscible	Miscible
Chloroform	Miscible	Miscible
Dichloromethane	Miscible	Miscible
Hexachloroethane	Sol.	Sol.
Bromoform	Miscible	Miscible
Iodoform	Slightly sol.	Slightly sol.
Ethyl bromide	Moderately sol.	Very sol.
Methylene iodide	Insol.	Insol.
Ether	Miscible	Miscible
Ethyl alcohol	Miscible	Miscible
Methanol	Miscible	Miscible
Ethylene glycol monobutyl ether	Miscible	Miscible
Glycerol	Insol.	Insol.
Acetone	Miscible	Miscible
Cane sugar	Insol.	Very slightly sol.
Cellulose acetate	Insol.	Insol.
Nitrocellulose (½ sec.)	Insol.	Insol.
Urea	Slightly Insol.	Slightly Insol.
Thiourea	Insol.	Insol.
Acetamide	Very slightly sol.	Very slightly sol.
Theobromine	Very sol.	Slightly sol.
Sulfonal	Slightly sol.	Moderately sol.
Trional	Slightly sol.	Very sol.
Dimethylglyoxime	Insol.	Insol.
Aromatic and Ring Compounds		
Benzene	Miscible	Miscible
Diphenyl	Moderately sol.	Very sol.
Naphthalene	Very sol.	Very sol.
Anthracene	Very slightly sol.	Very slightly sol.
Xylene	Miscible	Miscible
Chlorobenzene	Miscible	Miscible
Iodobenzene	Miscible	Miscible
α-Chloronaphthalene	Miscible	Miscible
α-Bromonaphthalene	Miscible	Miscible
Tribromophenol	Very sol.	Slightly sol.
Nitrobenzene	Miscible	Miscible
Azobenzene	Very sol.	Very sol.
Aniline	Insol.	Miscible
Acetanilide	Moderately sol.	Very slightly sol.
Antipyrine	Very slightly sol.	Slightly sol.

TABLE 8.22.—*Continued*

SOLUTE	$C_2Cl_3F_3$	$C_2Cl_4F_2$
Aromatic and Ring Compounds—Continued		
Diphenylamine	Insol.	Very sol.
Quinaldine	Miscible	Miscible
Methylene blue	Insol.	Insol.
Indigo	Very slightly sol.	Insol.
Phenol	Very slightly sol.	Very slightly sol.
Benzyl alcohol	Miscible	Miscible
Resorcinol	Insol.	Insol.
Benzil	Moderately sol.	Moderately sol.
Diphenyl carbinol	Moderately sol.	Very sol.
Thymol	Very sol.	Very sol.
Camphor	Very sol.	Very sol.
Benzophenone	Very sol.	Very sol.
Anthraquinone	Insol.	Slightly sol.
Phenolphthalein	Insol.	Insol.
p-Nitrobenzoylacetoacetic ester	Moderately sol.	Very sol.

Latent heat of vaporization at B. P.	78 cal./g.
Specific gravity at B. P.	1.004
Surface tension at −30° C	17–18 dynes/cm.
Index of refraction at 20° C	1.255

Vapor pressure:

Temperature °F	*Vapor Pressure (p.s.i.a.)*
70	77.2
100	124.7
130	192.3

$$\log_{10} P \text{ (pounds absolute)} = 5.7649 - \frac{2053.7}{t°\mathrm{F} + 459.6}$$

Solubility:

	Weight % CH_3CHF_2	
Solvent	*0°C*	*27.5° C*
Water	0.54	0.25
20% NaOH solution	—	0.04
25% NaCl solution	0.13	0.06
34.5% HCl solution	—	0.19

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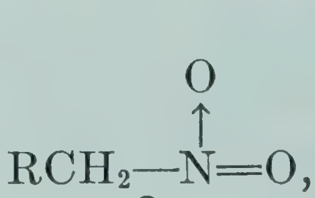
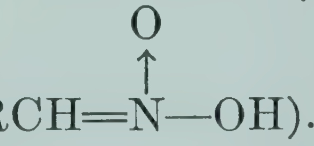
13. Booth, H. S., Mong, W. L., and Burchfield, P. E., *Ind. Eng. Chem.*, **24,** 328 (1932).

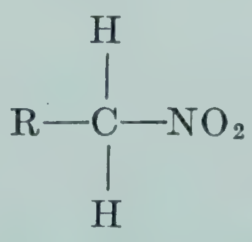
Chapter 9

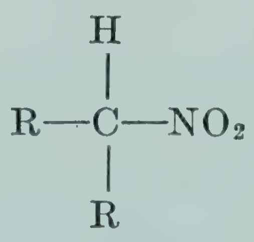
The Nitroparaffins

This class of compounds, introduced on a commercial scale about ten years ago, was originally prepared by Victor Meyer in 1872. Taking up the work of Meyer, Henry in 1895 experimented with and wrote about them, but succeeded in arousing little interest in these compounds at that time. They remained laboratory curiosities for many years.

About 1930 with the support of the Commercial Solvents Corporation, Haas[1] of Purdue undertook work on the nitroparaffins and evolved a method of preparing them by direct nitration. This method required five years to reach perfection, at which time Commercial Solvents Corporation obtained exclusive patent rights. Over 700 derivatives of the nitroparaffins were developed by 1940, and this date also marks the beginning of the commrecial production of the four lowest members of the series: nitromethane, nitroethane, 1-nitropropane, and 2-nitropropane.

The structure of the primary nitroparaffins is  $RCH_2—\overset{\overset{O}{\uparrow}}{N}=O$, which will form nitronic acid in the presence of water  $(RCH=\overset{\overset{O}{\uparrow}}{N}—OH)$. This will form the sodium salt in the presence of sodium hydroxide. The acids of these compounds can be regenerated with carbon dioxide. These compounds owe their peculiar behavior to the hydrogen atom attached to the nitro-bound carbon atoms of both the primary and secondary paraffins.





The nitroparaffins are saturated aliphatic compounds made by reacting petroleum hydrocarbons with nitric acid. The lower aliphatic nitroparaffins, such as nitromethane, nitroethane, 1-nitropropane, and 2-nitropropane, are colorless, nonhygroscopic liquids with a mild odor. Nitromethane is immiscible with even the low-boiling petroleum hydrocarbons; 1- and 2-nitropropane are miscible with petroleum naphtha, and nitroethane depends for its miscibility upon the boiling range of the hydrocarbon[2].

SOLVENT COMPOSITION FOR A STOCK SOLUTION OF CELLULOSE ACETATE[3]

	SOLVENT COMPOSITION		
	Concentrated Stock Solution	Thinner	Lacquer at Spraying Viscosity
1-Nitropropane	55%	15%	35%
Butanol	10	20	15
Ethyl alcohol	10	20	15
Toluene	25	45	35

SOLVENT COMPOSITION FOR A STOCK SOLUTION OF CELLULOSE TRIACETATE[3]
(43.5% Acetyl Radical)

	SOLVENT COMPOSITION		
	Concentrated Stock Solution	Thinner	Lacquer at Spraying Viscosity
1-Nitropropane	45%	45%	45%
Tetrachloroethane	30	—	10
Ethyl alcohol	25	25	25
Toluene	—	30	20

SOLVENT COMPOSITION FOR STOCK SOLUTION OF CELLULOSE ACETOBUTYRATE[3]
(31% Acetyl Radical and 16% Butyryl Radical)(3)

	SOLVENT COMPOSITION		
	Concentrated Stock Solution	Thinner	Lacquer at Spraying Viscosity
1- or 2-Nitropropane	45%	5%	25%
Butanol	5	15	10
Ethyl alcohol	15	15	15
Toluene	35	65	50

The nitroparaffins are medium boilers, have strong solvent power and a slow rate of evaporation, lying between those of toluene and butyl acetate. Their mutual solubility with water is very low. However, they will dissolve a wide range of substances, such as oil and spirit-soluble dyes, fats, waxes, nitrocellulose, resins, and the vinyl acetate-chloride resins. After mixing these solvents with at least 20 per cent of alcohol, they will dissolve cellulose acetate, cellulose acetopropionate, and acetobutyrate. The nitroparaffins are used as solvents for nitrocellulose, cellulose ethers, cellulose mixed ethers, vinyl copolymer resins, and certain types of synthetic rubbers, such as "Hycar OR". They are also used for their selective solvency in paint and varnish removers. Table 9.1 gives the solubility of a large number of substances in 1- and 2-nitropropane.

TABLE 9.1. SUBSTANCES SOLUBLE AND INSOLUBLE IN 1- AND 2-NITROPROPANE[4]

SOLUBLE SUBSTANCES[a]

- Waxes
  - Bayberry
  - Ceresin (SS)
  - Japan (SS)
  - Spermaceti (SS)
- Natural Resins and Gums
  - Barbados Manjak No. 84 (SS)
  - Dammar (PS)
  - Dammar (dewaxed) (SA)
  - Kauri white (SA)
  - Manila (SA)
  - Pontianak (SA)
  - Rosin (SS)
- Tars and Pitches
  - Blown asphalt (SS)
  - Bone pitch (SS)
  - Gilsonite (SS)
  - Petroleum asphalt (SS)
  - Refined coal tar (SS)
  - Road tar
- Synthetic Resins
  - Arochlor 1242
  - Bakelite
  - Beckacite
  - Durez
  - Ester gum
  - Glyptal 2471
  - Mowalith N
  - Paraplex 5B
  - Pliaflex
  - Rezyl 14
  - Rezyl 19
  - Rezyl 114 (SS)
  - Santolite MH
  - Santolite MHP
  - Teglac 65
  - Uformite
  - Vinylite H
  - Vinylite HH-44 (SS)
- Coating Materials
  - Benzylcellulose
  - Cellulose acetate (SA)
  - Cellulose acetobutyrate
  - Cellulose acetopropionate
  - Chlorinated rubber
  - Ethylcellulose
  - Nitrocellulose
- Dyes
  - Oil-soluble
  - Spirit-soluble (SS)
- Organic Chemicals
  - Acetic acid
  - Acetone
  - Aniline
  - Benzene
  - Butanol
  - Butyl acetate
  - Butyl butyrate
  - Butyl lactate
  - Butyl propionate
  - Butyric acid
  - Cottonseed oil fatty acids
  - Dibutyl phthalate
  - Ethyl alcohol
  - Ethyl acetate
  - Ethyl ether
  - Ethylpropylacrolein
  - Isopropyl alcohol
  - Maleic anhydride
  - Mesityl oxide
  - Naphtha
  - Naphthalene
  - Phenol
  - Phthalic anhydride
  - Picric acid
  - Ricinoleic acid
  - Toluene
  - Tributyl phosphate
- Oils and Fats
  - Castor oil
  - Coconut oil
  - Lanolin (SS)
  - Linseed oil
  - Petroleum ether
  - Petroleum oil
  - Soybean oil
  - Tung oil

INSOLUBLE SUBSTANCES

- Waxes
  - Beeswax
  - Candelilla
  - Carnauba
  - Montan
  - Ozocerite
  - Paraffin
- Natural Resins and Gums
  - Batu
  - Boea
  - Chicle
  - Congo (dark amber)
  - East India
  - Shellac
- Tars and Pitches
  - Cottonseed pitch (m.p. 59°C.)
  - Cottonseed pitch (m.p. 71°C.)
  - Mixed pitch
  - Paving pitch
  - Roofing pitch
  - Soft coal
- Coating Materials
  - Alkagel
  - Casein
  - Dextrin
  - Egg albumen
  - Gelatin
  - Methylcellulose
  - Zein (cured)
  - Zein (uncured)
- Dyes
  - Water-soluble
- Organic Chemicals
  - Adipic acid
  - Aluminum stearate
  - Ammonium linoleate
  - Anthracene
  - Citric acid
  - Fumaric acid
  - Glucose
  - Glycerol
  - Glycerol boriborate
  - Hydroquinone
  - Maleic acid
  - Oxalic acid
  - Pyrogallic acid
  - Salicylic acid
  - Sebacic acid
  - Sodium alginate
  - Starch, corn
  - Starch, potato
  - Stearic acid
  - Succinic acid
  - Sugar
  - Tannic acid
  - Tartaric acid

[a] Soluble to the extent of at least 10 grams per 100 ml., unless marked by letters in parentheses as follows: SA = soluble in presence of alcohols; SS = soluble but less than 10 grams per 100 ml.; PS = only part of substance soluble.

The possibilities of these compounds are unlimited, in the opinion of Gabriel[4] and others. The Commercial Solvents Corporation, impressed with their wide and far-reaching importance, has compared their discovery with that of aniline dye mauve by William Henry Perkin in 1856, and claims that these compounds will similarly give rise to a new field of organic chemistry. Gabriel has also prepared several interesting chemical "trees" illustrating the derivatives of these products (Figs. 9.1, 9.2 and 9.3).

TABLE 9.2. EVAPORATION RATES OF NITROPARAFFINS AND LACQUER SOLVENTS[4]

SOLVENT	B.P., °C	EVAPN. RATE[a]	SOLVENT	B.P., °C	EVAPN. RATE[a]
Acetone	56.1	720	Nitroethane	114.0	145
Ethyl acetate	77.1	525	2-Nitropropane	120.0	124
Methyl ethyl ketone	79.6	465	Butyl acetate	126.5	100
Dioxane	101.5	215	1-Nitropropane	132.0	100
Ethyl alcohol	78.1	203	Methyl Cellosolve	124.3	55
Toluene	110.8	195	Butyl alcohol	117.7	45
Nitromethane	101.0	180	Ethyl lactate	154.0	22
			Diacetone alcohol	166.0	15

[a] Compared to butyl acetate as 100.

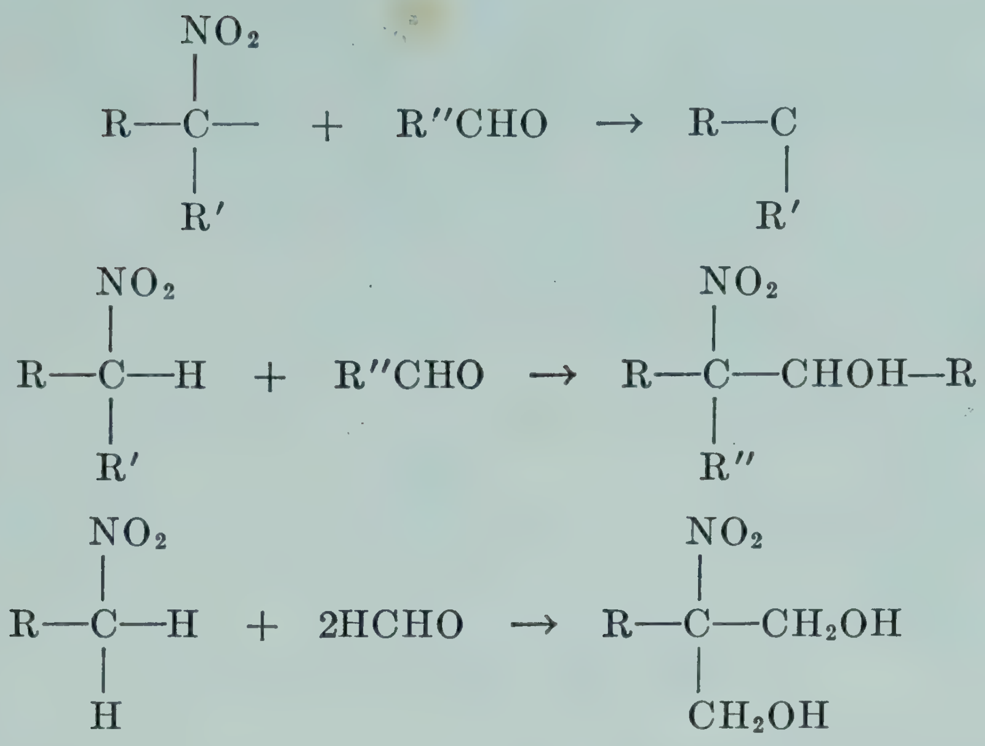
Bogin and Wampner[2] have made some interesting studies and useful tabulations of their results. Table 9.2 lists the evaporation rates of a number of solvents compared with those of the nitroparaffins. Additional technical data are given in Tables 9.3–9.13.

Ericsson[5] in a number of tables, compares the nitroparaffins with other solvents.

2-Nitropropane ($CH_3CHNO_2CH_3$). Having but one available hydrogen atom, the condensation product, when reacted with an aldehyde, can only be a monohydroxy nitrocompound. This is also true of chlorine, where the reaction gives 2-chloro-2-nitropropane. This nitroparaffin has outstanding solvent strength and although but a recently introduced solvent, it is finding use in the manufacture of protective coatings, such as vinyl acetate-vinyl chloride copolymers, cellulose acetate, cellulose mixed ester, and vinyl acetal resins. It also finds use in adhesives and printing inks. (See Table 9.3 for physical properties.)

THE NITROALCOHOLS

At the same time that Henry[6] worked with and wrote about the nitroparaffins (1895) he also obtained, in cooperation with Maas, Mousset, Pauwels, and Shaw, the nitroparaffin derivatives (nitroalcohols) by condensing aldehydes with them. Haas later continued the investigation of these compounds and together with Vanderbilt[7] prepared a large number of nitroalcohols.



$$R-\underset{R'}{\overset{NO_2}{\overset{|}{\underset{|}{C}}}}- \;+\; R''CHO \;\rightarrow\; R-\underset{R'}{\underset{|}{C}}$$

$$R-\underset{R'}{\overset{NO_2}{\overset{|}{\underset{|}{C}}}}-H \;+\; R''CHO \;\rightarrow\; R-\underset{R''}{\overset{NO_2}{\overset{|}{\underset{|}{C}}}}-CHOH-R$$

$$R-\underset{H}{\overset{NO_2}{\overset{|}{\underset{|}{C}}}}-H \;+\; 2HCHO \;\rightarrow\; R-\underset{CH_2OH}{\overset{NO_2}{\overset{|}{\underset{|}{C}}}}-CH_2OH$$

These compounds, in the opinion of their investigators, possess excellent solvent power for many substances because of the presence of an alcohol and a nitro-group. They are used as mild oxidizing agents, surface-active and flotation agents, in the synthesis of emulsifiers, as plasticizers, high-

(Text continued on page 391)

TABLE 9.3. PHYSICAL CONSTANTS OF NITROPARAFFINS[2]

FORMULA	NITROMETHANE CH_3NO_2	NITROETHANE $CH_3CH_2NO_2$	1-NITROPROPANE $CH_3CH_2CH_2NO_2$	2-NITROPROPANE $CH_3CHNO_2CH_3$
Mol. weight	61	75	89	89
Boiling point, °C	101	114	132	120
Freezing point, °C	−29	−90	−108	−93
Flash point (Tagliabue open cup), °F	95	82	93	75
Index of refraction, 20° C	1.3817	1.3917	1.4015	1.3941
Specific gravity, 20/20° C	1.139	1.052	1.003	0.992
Weight per U. S. gal., lb.	9.5	8.8	8.4	8.3
Color	Water-white	Water-white	Water-white	Water-white
Odor	Mild	Mild	Mild	Mild
Soly. in 100 cc. water, cc.	9.10	4.5	1.4	1.7
Soly. of water in 100 cc. nitroparaffin, cc.	2.2	0.9	0.5	0.6
Vapor pressure at 20° C, mm. Hg	27.8	15.6	7.5	12.9
pH 0.01 *M* aq. soln.	6.12	5.20	5.61	5.33
pH water satd. with nitroparaffin	4.01	3.85	4.33	4.29
pH nitroparaffin satd. with water	4.82	3.75	4.06	3.00
Surface tension at 20° C, dynes/cm.	37	31	30	—
Evaporation rate (1-butanol)	4	3	2	2.5

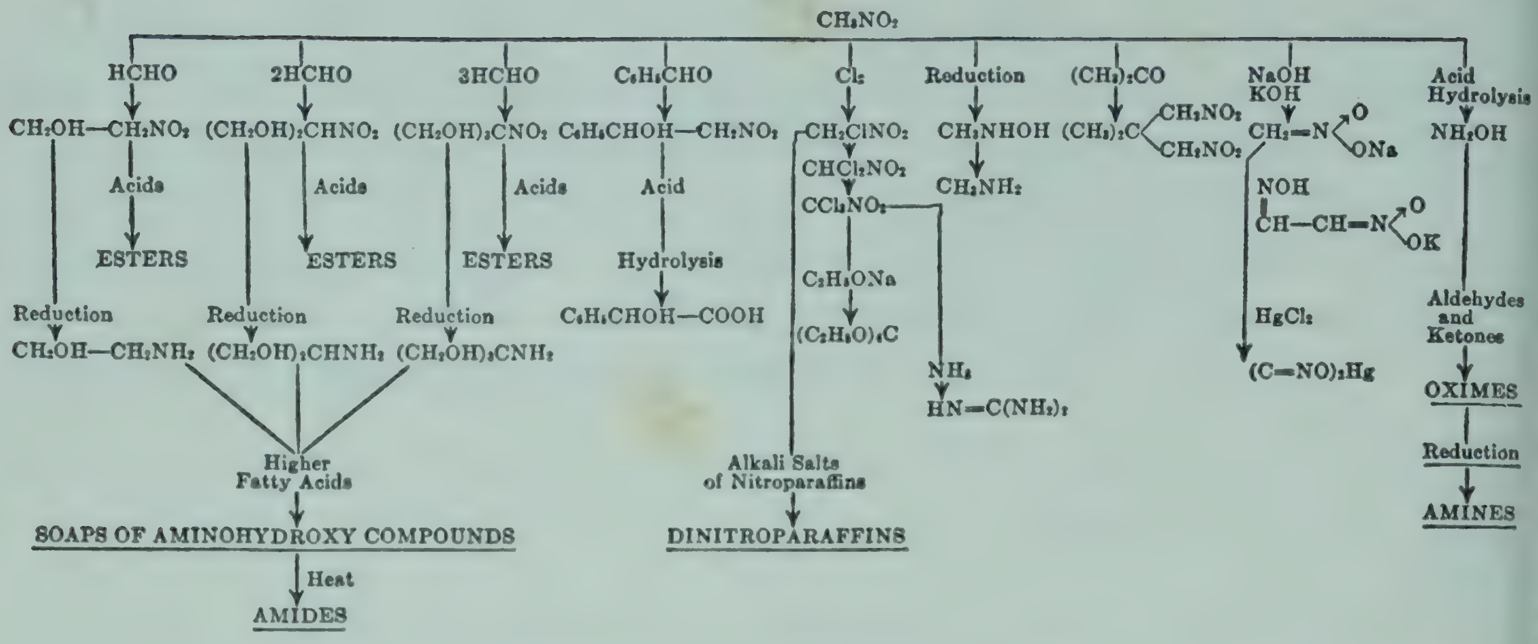

CH_3NO_2
HCHO
2HCHO
3HCHO
C_6H_5CHO
Cl_2
Reduction
$(CH_3)_2CO$
NaOH KOH
Acid Hydrolysis
$CH_2OH—CH_2NO_2$
$(CH_2OH)_2CHNO_2$
$(CH_2OH)_3CNO_2$
$C_6H_5CHOH—CH_2NO_2$
CH_2ClNO_2
$CHCl_2NO_2$
CCl_3NO_2
CH_3NHOH
CH_3NH_2
$(CH_3)_2C(CH_2NO_2)_2$
$CH_2=N(O)ONa$
NH_2OH
Acids
ESTERS
Acid
Hydrolysis
$C_6H_5CHOH—COOH$
C_2H_5ONa
$(C_2H_5O)_4C$
NH_3
$HN=C(NH_2)_2$
NOH
$CH—CH=N(O)OK$
$HgCl_2$
$(C=NO)_2Hg$
Aldehydes and Ketones
OXIMES
Reduction
AMINES
$CH_2OH—CH_2NH_2$
$(CH_2OH)_2CHNH_2$
$(CH_2OH)_3CNH_2$
Higher Fatty Acids
SOAPS OF AMINOHYDROXY COMPOUNDS
Heat
AMIDES
Alkali Salts of Nitroparaffins
DINITROPARAFFINS

Figure 9-1. Nitromethane Tree

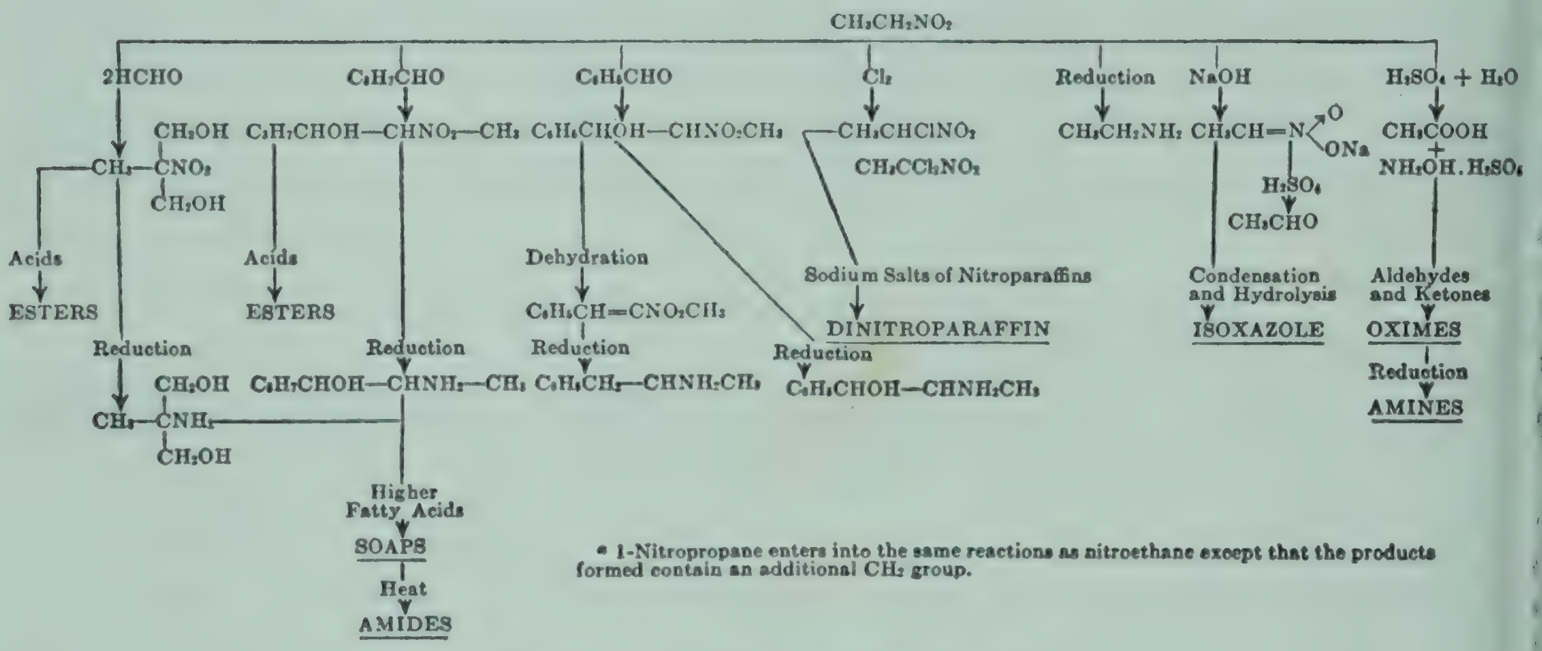

$CH_3CH_2NO_2$
2HCHO
C_3H_7CHO
C_6H_5CHO
Cl_2
Reduction
NaOH
$H_2SO_4 + H_2O$
$CH_3—C(CH_2OH)_2NO_2$
$C_3H_7CHOH—CHNO_2—CH_3$
$C_6H_5CHOH—CHNO_2CH_3$
$CH_3CHClNO_2$
$CH_3CCl_2NO_2$
$CH_3CH_2NH_2$
$CH_3CH=N(O)ONa$
H_2SO_4
CH_3CHO
$CH_3COOH + NH_2OH.H_2SO_4$
Acids
ESTERS
Dehydration
$C_6H_5CH=CNO_2CH_3$
Sodium Salts of Nitroparaffins
DINITROPARAFFIN
Condensation and Hydrolysis
ISOXAZOLE
Aldehydes and Ketones
OXIMES
Reduction
AMINES
$CH_3—C(CH_2OH)_2NH_2$
$C_3H_7CHOH—CHNH_2—CH_3$
$C_6H_5CH_2—CHNH_2CH_3$
$C_6H_5CHOH—CHNH_2CH_3$
Higher Fatty Acids
SOAPS
Heat
AMIDES

Figure 9-2. Nitroethane Tree[a]

[a] 1-Nitropropane enters into the same reactions as nitroethane except that the products formed contain an additional CH_2 group.

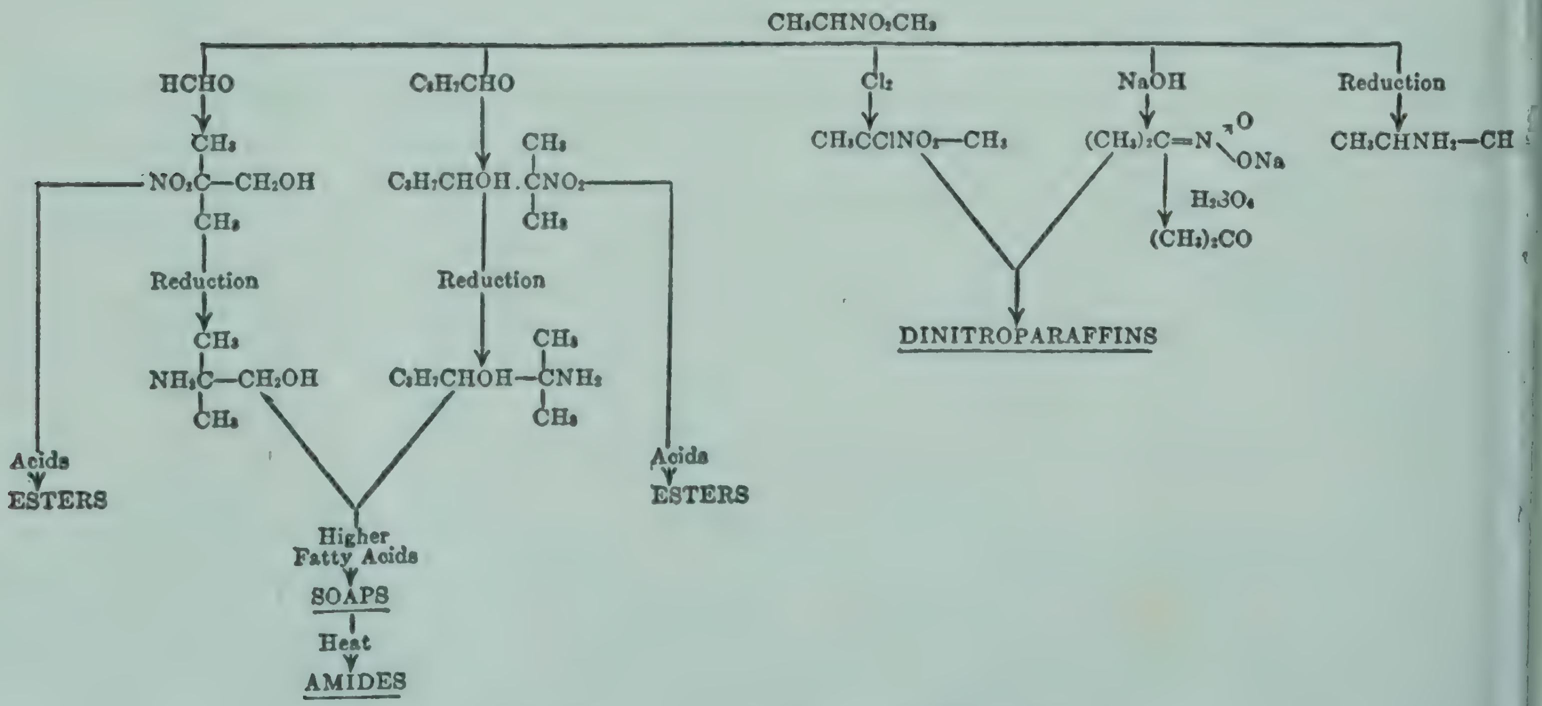
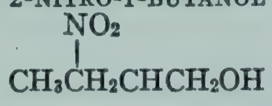
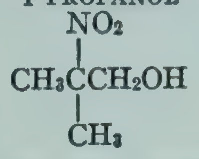
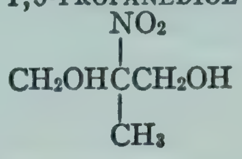

$CH_3CHNO_2CH_3$
HCHO
C_3H_7CHO
Cl_2
NaOH
Reduction
$NO_2C(CH_3)_2—CH_2OH$
$C_3H_7CHOH.CNO_2(CH_3)_2$
$CH_3CClNO_2—CH_3$
$(CH_3)_2C=N(O)ONa$
H_2SO_4
$(CH_3)_2CO$
$CH_3CHNH_2—CH$
DINITROPARAFFINS
$NH_2C(CH_3)_2—CH_2OH$
$C_3H_7CHOH—C(CH_3)_2NH_2$
Acids
ESTERS
Higher Fatty Acids
SOAPS
Heat
AMIDES

Figure 9-3. 2-Nitropropane Tree

TABLE 9.4. PHYSICAL CONSTANTS OF NITROPARAFFIN DERIVATIVES[2]

FORMULA	2-NITRO-1-BUTANOL  $\mathrm{CH_3CH_2\overset{NO_2}{\overset{\vert}{C}}HCH_2OH}$	2-NITRO-2-METHYL-1-PROPANOL  $\mathrm{CH_3\underset{CH_3}{\underset{\vert}{\overset{NO_2}{\overset{\vert}{C}}}}CH_2OH}$	2-NITRO-2-METHYL-1,3-PROPANEDIOL  $\mathrm{CH_2OH\underset{CH_3}{\underset{\vert}{\overset{NO_2}{\overset{\vert}{C}}}}CH_2OH}$
Mol. weight	119	119	135
Melting point, °C	−47 to −48	90–91	147–149
Boiling point at 10 mm., °C	105	94.5–95.5	Decomposes
pH 0.1 *M* aqueous soln.	4.51	5.12	5.42
Soly. in 100 cc. water at 20°C, grams	20	350	80

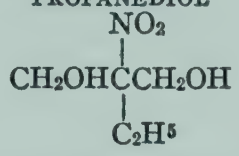
	2-NITRO-2-ETHYL-1,3-PROPANEDIOL  $\mathrm{CH_2OH\underset{C_2H^5}{\underset{\vert}{\overset{NO_2}{\overset{\vert}{C}}}}CH_2OH}$	TRIS(HYDROXYMETHYL) NITROMETHANE $\mathrm{NO_2C(CH_2OH)_3}$
Mol. weight	149	151
Melting point, °C	56–57	165–170
Boiling point at 10 mm., °C	Decomposes	Decomposes
pH 0.1 *M* aqueous soln.	5.48	5.61
Soly. in 100 cc. water at 20°C, grams	400	220

TABLE 9.5. SOLUBILITY AT 25°C OF CELLULOSE ACETOBUTYRATE IN MIXTURES OF 1-NITROPROPANE AND DILUENTS[2]

COMPN. OF SOLVENT MIXT., % BY VOL.					SOLUBILITY
1-Nitropropane	Toluene	Ethanol	Butanol	Butyl acetate	
100	—	—	—	—	Sol.
60	—	40	—	—	Sol.
50	—	50	—	—	Sol.
40	—	60	—	—	P. sol.[a]
70	30	—	—	—	P. sol.[a]
60	40	—	—	—	P. sol.[a]
40	30	30	—	—	Sol.
35	32.5	32.5	—	—	Sol.
35	25	40	—	—	Sol
35	40	25	—	—	Sol.
30	35	35	—	—	Sol.
30	45	25	—	—	Sol.
25	37.5	37.5	—	—	Sol.
50	25	—	25	—	Sol.
40	30	—	30	—	Sol.
30	35	—	35	—	P. sol.
50	—	—	—	50	P. sol.
40	—	30	—	30	Sol.
30	—	35	—	35	Insol.

[a] At somewhat higher temperatures the "partly soluble" mixtures dissolved the cellulose ester and the solutions remained homogeneous when the temperature was reduced.

TABLE 9.6. RESIN COMPATIBILITY[2]

RESINS COMPATIBLE WITH CELLULOSE ACETOBUTYRATE		50:50 MIXT. OF SANTOLITE MHP[a] WITH FOLLOWING RESINS	
Resin	Ratio Resin: ester	Resin	Ratio, Santolite MPH: resin
Santolite MS	4:1	Ester gum	2:1
Santolite MPH	4:1	Dammar	2:1
Rezyl 14	4:1	Rezyl 19	2:1
Rezyl 337-1	4:1	Rezyl 53	2:1
Rezyl 337-2	4:1	Rezyl 127	2:1
Superbeckacite 2000	3:1	Petrex A21	2:1
Vinsol	2:1	Beckosol 1323	2:1
Hercolyn	1.5:1	Superbeckacite 1001	2:1
Bakelite 4357	1.5:1	Teglac 15	2:1
		Staybelite A-1	2:1

[a] In some cases the Santolite MHP can be replaced by Rezyl 14, Rezyl 337-1, Santolite MS, or Bakelite 4357.

TABLE 9.7. FORMULATION OF CELLULOSE ACETOBUTYRATE, ACETATE, AND TRIACETATE LACQUER SOLVENTS[2]

SOLVENT CONSTITUENT	% COMPOSITION		
	Solvent for concd. stock soln.	Thinner	Solvent in lacquer at spraying viscosity
A. Cellulose Acetobutyrate			
1- or 2-Nitropropane	45	5	25
Butanol	5	15	10
Ethanol	15	15	15
Toluene	35	65	50
B. Cellulose Acetate			
1-Nitropropane	55	15	35
Butanol	10	20	15
Ethanol	10	20	15
Toluene	25	45	35
C. Cellulose Triacetate			
1-Nitropropane	45	45	45
Tetrachlorethane	30	—	10
Ethanol	25	25	25
Toluene	—	30	20

TABLE 9.8. DILUTION RATIOS OF 1-NITROPROPANE[a] SOLUTIONS OF CELLULOSE ACETOBUTYRATE[2]

COMPN. OF DILUENT, % BY VOL.	DILUTION RATIO	FINAL CONCN. OF CELLULOSE ACETOBUTYRATE, G./100 ML. OF VOLATILES
100 ethanol	3.3	7.0
100 toluene	2.1	4.5
70:30 ethanol:toluene	5.6	6.0
50:50 ethanol:toluene	9.6	4.2
30:70 ethanol:toluene	10+	2.5
100 butanol	2.0	6.5
70:30 butanol:toluene	3.5	8.5
50:50 butanol:toluene	5.4	6.0
30:70 butanol:toluene	10+	2.7
70:30 ethanol:naphtha	3.5	2.5
30:70 ethanol:naptha	3.0	2.5

[a] The values for 2-nitropropane are only slightly different.

TABLE 9.9. VISCOSITIES OF 5 PER CENT SOLUTIONS OF CELLULOSE ACETOBUTYRATE IN VARIOUS SOLVENT MIXTURES[2]

MIXT. NO.	COMPN. OF SOLVENT MIXT., % BY VOL.	VISCOSITY, CENTIPOISES
1	1-Nitropropane, 100	74.5
2	1-Nitropropane:ethyl alcohol, 60:40	69.0
	1-Nitropropane:ethanol:toluene	
3	60:20:20	57.0
4	30:35:35	55.0
5	20:40:40	55.0
6	20:25:55	47.0
7	20:50:30	65.0
8	15:40:45	55.0
9	15:25:60	47.0
10	10:45:45	Gelled
11	10:30:60	Partly gelled
	1-Nitropropane:butanol:toluene	
12	60:20:20	63.0
13	40:30:30	66.0
14	30:35:35	68.0
15	20:40:40	70.0
16	20:25:55	52.0
17	20:50:30	82.0
18	15:25:60	56.0
	Diacetone:ethyl acetate:toluene:acetone	
19	15:35:20:30	62.5

TABLE 9.10. DILUTION RATIOS OF 1-NITROPROPANE SOLUTIONS OF CELLULOSE ACETATE[2]*

MIXT. NO.	COMPN. OF DILUENT, % BY VOL.	DILUTION RATIO
	Ethanol:toluene	
1	20:80	1.2
2	30:70	3.0
3	50:50	5.9
4	100:0	2.3
	Ethanol:butanol:toluene	
5	12.5:12.5:75	0.7
6	15:15:70	3.1
7	20:20:60	4.0
8	25:25:50	4.2
9	30:30:40	4.0
10	40:40:20	2.8
11	50:50:0	2.1

* Combined acetic acid, 54.5 per cent; A.S.T.M. viscosity, 2.5–8 seconds; concentration at end point, 8 grams per 100 ml. volatiles.

TABLE 9.11. DILUTION RATIOS OF CELLULOSE ACETOPROPIONATE SOLUTIONS[2]

SOLVENT COMPN., % BY VOL.	DILUENT	DILUTION RATIO	FINAL CONCN. OF CELLULOSE ACETOPROPIONATE, G./100 ML. VOLATILES
1-Nitropropane	Toluene	3.5	3.5
1-Nitropropane:butanol, 66:33	Toluene	7.1	6.3
1-Nitropropane:butanol, 66:33	Xylene	3.8	6.7
Butyl acetate	Toluene	1.9	6.2
Butyl acetate:butanol, 66:33	Toluene	3.3	5.6
Butyl acetate:butanol, 66:33	Xylene	0.9	6.9

TABLE 9.12. DILUTION RATIOS OF FORMVAR SOLUTIONS[2]*

DILUENT	DILUTION RATIO	FINAL CONCN. OF FORMVAR, G./100 ML. OF VOLATILES
Toluene	1.25	6.7
Ethanol	0.95	7.7
Ethyl acetate	1.05	7.3
Methyl ethyl ketone	0.5	10.0
Butanol	1.2	6.8
Butyl acetate	0.7	8.8
Ethanol:toluene, 50:50	5.8	2.6
Ethanol:ethyl acetate, 50:50	1.3	6.5
Ethanol:methyl ethyl ketone, 50:50	1.1	7.2
Toluene:butanol, 50:50	>5.0	2.5
Toluene:ethyl acetate, 50:50	>5.0	2.5
Toluene:methyl ethyl ketone, 50:50	1.1	7.2

* Solvent composition, 90:10 1-nitropropane:ethanol.

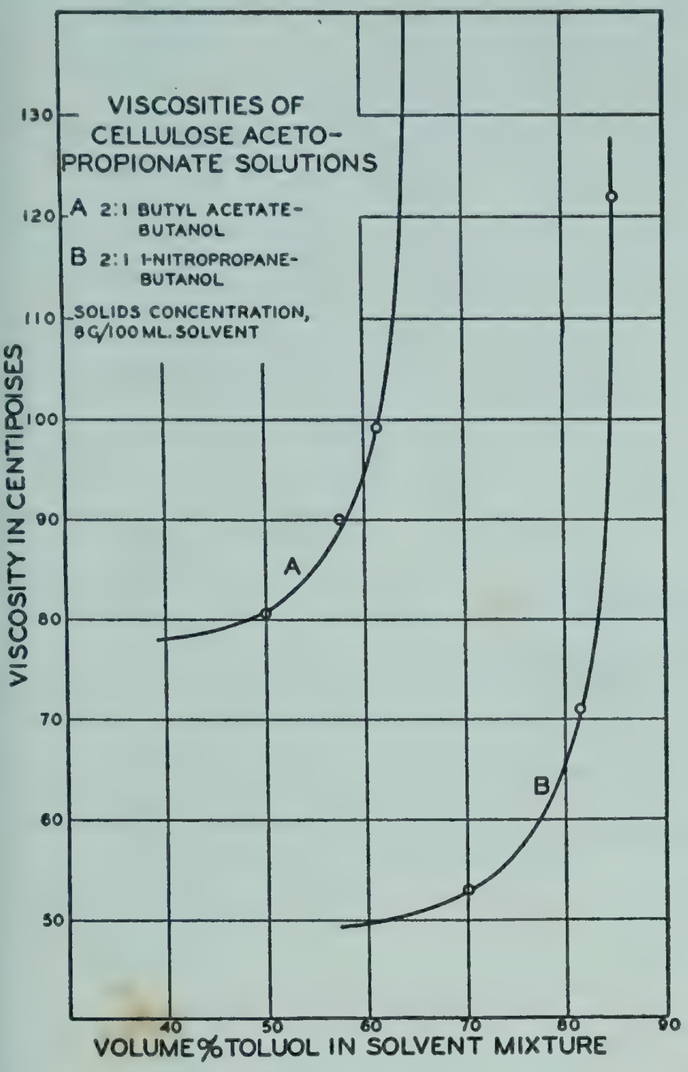


Figure 9-4.[2]

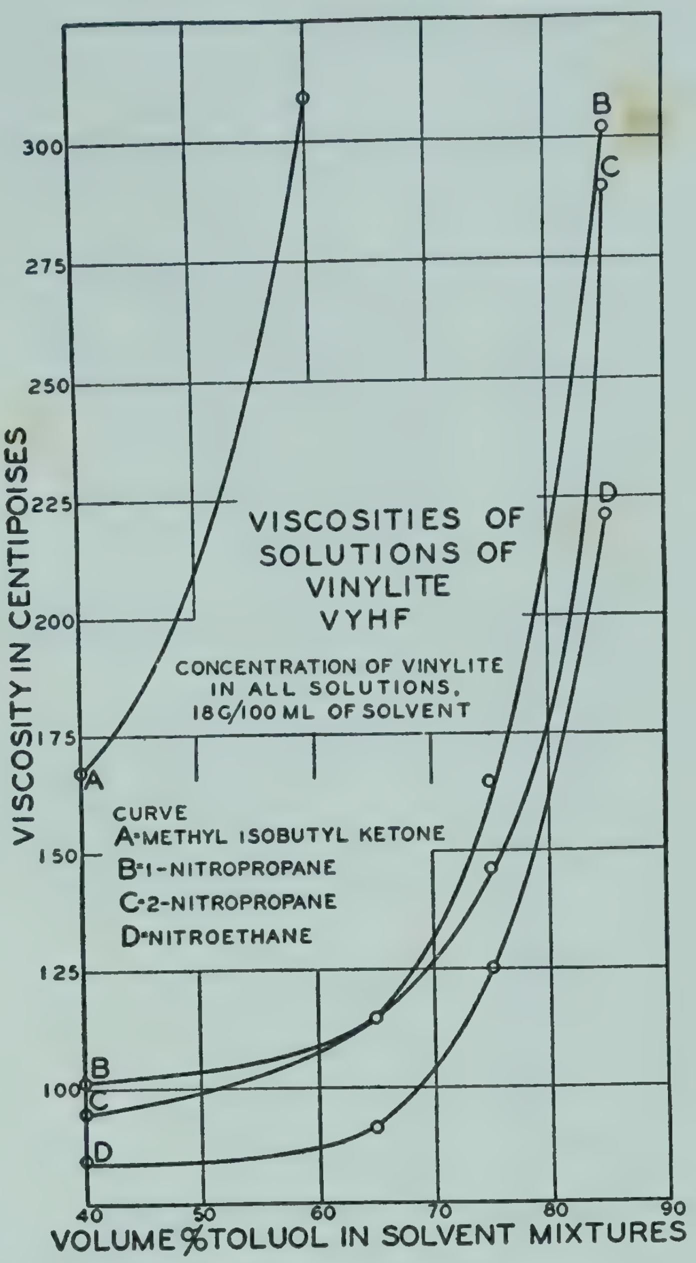


Figure 9-5.[2]

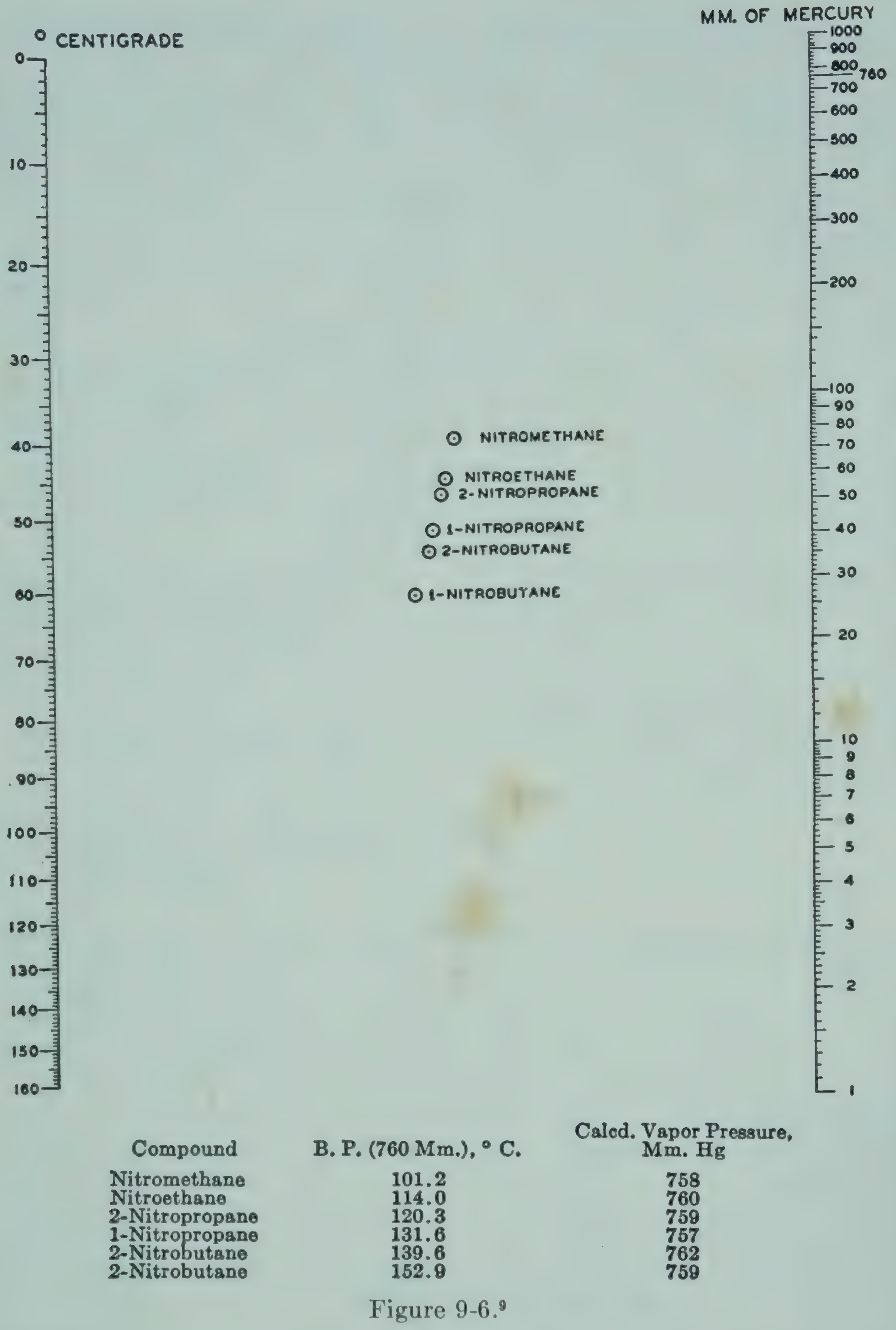
Table 9.13. Dilution Ratios of Nitrocellulose in Nitropropane Solvents[2]*

Solvent	Dilution ratio with following diluents:		
	Toluene	50:50 toluene:naphtha	Naphtha
1-Nitropropane	1.2	0.6	0.4
1-Nitropropane:butanol, 66:33	2.7	1.5	0.8
2-Nitropropane	1.3	0.6	0.3
2-Nitropropane:butanol, 66:33	3.0	1.4	0.7
2-Nitropropane:ethanol, 66:33	3.0	1.3	0.7

* Concentration, 8 grams per 100 ml. volatiles.

boiling solvents, zein solvent and as heat sensitizers for rubber latex. These nitroparaffin derivatives are also the bases for interesting possibilities in organic syntheses.

Schumacher and Hunt[8] have worked out detailed vapor-liquid equilibrium data for various binary and ternary systems of alcohol, nitromethane and water.



Compound	B. P. (760 Mm.), ° C.	Calcd. Vapor Pressure, Mm. Hg
Nitromethane	101.2	758
Nitroethane	114.0	760
2-Nitropropane	120.3	759
1-Nitropropane	131.6	757
2-Nitrobutane	139.6	762
2-Nitrobutane	152.9	759

Figure 9-6.[9]

A nomograph is included (Fig. 9.6) from which values accurate enough for many purposes can be read. This was constructed according to the method of Killeffer, except that the temperature scale was averaged from scales of nitromethane and 2-nitrobutane, which were found to differ somewhat. Over most of the range, pressures for a given temperature can be read within about 2 per cent of the value calculated from the corresponding equation.

TABLE 9.14. TYPICAL SOLUBILITY CHARACTERISTICS OF NITROPARAFFINS[5]

Materials Soluble in 1- and 2-Nitropropane

Glyptal resins
Vinylite resins
Cellulose esters
Cellulose ethers
Liquid organic acids
Alkyl esters and ethers
Aryl esters and ethers
Alcohols
Ketones
Aldehydes
Alkyl amines
Aryl amines
Buna N type rubbers
Vegetable fats and oils
Animal fats and oils
All low-boiling hydrocarbons and chlorinated hydrocarbons

Materials Insoluble in 1- and 2-Nitropropane

Inorganic acids and salts
Metallic soaps
Solid organic acids
Sugars
Most natural resins
Alkanol amines
Proteinlike materials
Natural rubber
Buna S type rubbers
High-boiling hydrocarbons

TABLE 9.15. SOLVENTS FOR CELLULOSE ACETATE BUTYRATE[a] AND CELLULOSE ACETATE[b] [5]

CELLULOSE ACETATE BUTYRATE		CELLULOSE ACETATE	
Solvent	Evapn. rate[c]	Solvent	Evapn. rate[c]
Acetone	720	Methyl acetate	1040
Ethylene dichloride	575	Acetone	720
Ethyl acetate	525	Ethyl acetate	525
Methyl ethyl ketone	465	Methyl ethyl ketone	465
Dioxane	215	Dioxane	215
Nitromethane	180	Nitromethane	180
Nitroethane	145	Nitroethane	145
2-Nitropropane	124	Mesityl oxide	87
1-Nitropropane	100	Tetrachloroethane	75
Tetrachloroethane	75	Methyl Cellosolve	55
Ethylene chlorohydrin	45	Ethylene chlorohydrin	46
Diacetone (acetone-free)	15	Methyl Cellosolve acetate	40
		Methyl lactate	29
		Ethyl lactate	22
		Diacetone (acetone-free)	15

[a] Acetyl content 31%, butyryl content 16%.
[b] Acetyl content 37–42%.
[c] Butyl acetate = 100.

TABLE 9.16. PHYSICAL CONSTANTS OF NITROALCOHOLS[7]

NITROALCOHOL	PREPARED FROM		B. P. AT 10 MM., °C	SPECIFIC GRAVITY, d_4^{25}	REFRACTIVE INDEX, n_D^{20}	% NITROGEN	
	Nitroparaffin	Aldehyde				Theoretical	Found
2-Nitro-1-propanol	$EtNO_2$	HCHO	99	1.1841	1.4379	—	—
3-Nitro-2-butanol	$EtNO_2$	CH_3CHO	92	1.1296	1.4420	—	—
2-Nitro-3-hexanol	$EtNO_2$	C_3H_7CHO	108	1.0575	1.4480	9.52	9.42, 9.45
2-Nitro-1-butanol	1-$PrNO_2$	HCHO	105	1.1332	1.4390	—	—
3-Nitro-2-pentanol	1-$PrNO_2$	CH_3CHO	100	1.0818	1.4419	—	—
3-Nitro-4-heptanol	1-$PrNO_2$	C_3H_7CHO	115	1.0275	1.4460	8.70	8.65, 8.72
2-Methyl-2-nitro-1-propanol	2-$PrNO_2$	HCHO	89.5–90[a]	—	—	—	—
3-Methyl-3-nitro-2-butanol	2-$PrNO_2$	CH_3CHO	90	1.1021	1.4469	10.53	10.58, 10.72
2-Methyl-2-nitro-3-hexanol	2-$PrNO_2$	C_3H_7CHO	109	1.0405	1.4499	8.70	8.55, 8.69
2-Nitro-1-pentanol	1-$BuNO_2$	HCHO	117	1.0818	1.4405	—	—
3-Nitro-2-hexanol	1-$BuNO_2$	CH_3CHO	112	1.0487	1.4438	—	—
5-Nitro-4-octanol	1-$BuNO_2$	C_3H_7CHO	124	1.0394	1.4463	8.00	7.81, 7.94
2-Methyl-2-nitro-1-butanol	2-$BuNO_2$	HCHO	98	1.1047	1.4468	10.53	10.51, 10.53
3-Methyl-3-nitro-2-pentanol	2-$BuNO_2$	CH_3CHO	100	1.1157	1.4518	9.52	9.39, 9.42
3-Methyl-3-nitro-4-heptanol	2-$BuNO_2$	C_3H_7CHO	119	1.0281	1.4532	8.00	7.81, 7.93
3-Methyl-2-nitro-1-butanol	1-Iso-$BuNO_2$	HCHO	111	1.0886	1.4430	—	—
4-Methyl-3-nitro-2-pentanol	1-Iso-$BuNO_2$	CH_3CHO	96–98	1.0599	1.4477	—	—
2-Methyl-3-nitro-4-heptanol	1-Iso-$BuNO_2$	C_3H_7CHO	111	1.0140	1.4485	8.00	7.98, 8.11
2-Methyl-3-nitro-4-heptanol (stereoisomer)	1-Iso-$BuNO_2$	C_3H_7CHO	121 (53[a])	—	—	8.00	7.91, 8.12
2-Methyl-2-nitro-1,3-propanediol	$EtNO_2$	2HCHO	149–150[a]	—	—	—	—
2-Ethyl-2-nitro-1,3-propanediol	1-$PrNO_2$	2HCHO	56[a]	—	—	—	—
2-Nitro-2-propyl-1,3-propanediol	1-$BuNO_2$	2HCHO	81–81.5[a]	—	—	—	—
2-Nitro-2-isopropyl-1,2-propanediol	1-Iso-$BuNO_2$	2HCHO	87–88[a]	—	—	—	—
2-Amino-2-ethyl-1,3-propanediol	—	—	—	—	—	11.76	11.56, 11.69
2-Amino-2-propyl-1,3-propanediol	—	—	—	—	—	10.52	10.25, 10.32
2-Amino-2-isopropyl-1,3-propanediol	—	—	—	—	—	10.52	10.35, 10.38

[a] Melting point.

ISOPROPYL ALCOHOL-WATER				NITROMETHANE-WATER				NITROMETHANE-ISOPROPYL ALCOHOL	
% alcohol in liquid	% alcohol in vapor	% 2-propanol by wt.	Refractive index (20°C.)	% water in liquid	% water in vapor^a	% water	Refractive index (20°C.)	% alcohol in liquid	% alcohol in vapor
91.3	89.7	5.00	1.337	2.5	13.0	0.72	1.3813	2.90	17.3
90.0	89.0	10.00	1.342	5.4	19.7	9.99	1.3811	6.40	32.0
88.4	87.9	15.00	1.346	8.2	22.0	1.78	1.3805	11.9	42.7
86.8	87.0	20.00	1.351	11.5	22.8	2.03	1.3802	17.5	48.5
84.7	85.9	25.00	1.354	16.0	23.6	3.04^b	1.3800	17.8	49.3
82.5	84.9	30.00	1.358	19.9	23.6	3.97^b	1.3800	24.2	53.6
80.0	83.9	35.00	1.361	27.9	23.6	5.00^b	1.3800	24.7	54.3
78.0	83.3	40.00	1.364	34.6	23.6	87.16^b	1.3400	31.9	57.4
75.8	82.5	45.00	1.366	44.2	23.5	87.87^b	1.3400	41.5	60.1
73.5	82.2	50.00	1.368	49.7	23.5	88.85^b	1.3400	42.1	61.8
72.7	81.8	55.00	1.370	56.6	23.3	89.93	1.3395	47.6	63.7
68.0	80.9	60.00	1.371	68.5	23.5	90.93	1.3390	47.9	63.0
65.0	80.5	65.00	1.373	75.3	23.7	91.98	1.3385	53.4	6.55
62.8	80.1	70.00	1.3745	78.0	24.0	92.98	1.3380	58.1	66.4
61.6	79.9	80.00	1.3765	81.2	25.2	94.07	1.3371	58.6	66.9
59.3	80.0	90.00	1.3775	85.0	27.2			52.5	67.9
58.1	79.7	100.00	1.3776	87.3	28.8			66.6	69.3
52.0	79.2			91.7	36.1			66.8	69.4
44.0	78.8			92.6	39.2			70.5	71.2
41.8	78.3			95.4	52.5			74.3	73.1
33.0	77.7							77.5	75.2
24.0	77.0							78.5	75.5
17.3	75.2							81.7	77.5
17.5	74.8							85.1	79.9
11.6	71.8							88.1	82.4
10.7	70.8							91.0	85.0

---

[a] These data show the vapor to be slightly richer in water than do the data of Fowler and Hunt. The authors were aware of this at the time of the experimentation, and since the present data were obtained repeatedly they must take precedence over the former data.

[b] Two phases; the data are for the water phase.

TABLE 9.18. BOILING AND FLASH POINTS OF NITROPARAFFINS COMPARED WITH COMMON HYDROCARBONS, KETONES, AND ESTERS[5]

	BOILING POINT, °C.	FLASH POINT (TAG OPEN CUP), °F
Nitromethane	101.2	112
Nitroethane	114.0	106
2-Nitropropane	120.3	103
1-Nitropropane	131.6	120
Toluene	110.8	56
Naphtha, high-boiling	103–142[a]	<70
Dioxane	101.5	69
Methyl ethyl ketone	79.6	66
Methyl isobutyl ketone	116.0	98
Butyl acetate	126.5	102

[a] Distillation range.

TABLE 9.19. DATA FOR THE TERNARY SYSTEM ISOPROPYL ALCOHOL-NITROMETHANE-WATER[8]

EQUILIBRIUM DATA						SOLUBILITY DATA, % AT 25°C.		
Liquid Data, %			Vapor Data, %					
Isopropyl alcohol	Water	Nitromethane	Isopropyl alcohol	Water	Nitromethane	Isopropyl alcohol	Water	Nitromethane
80.0	10.0	10.0	73.8	8.0	18.2	0.0	89.0	11.0
80.0	14.0	6.0	78.3	9.5	12.2	13.6	73.5	12.9
80.0	6.0	14.0	73.6	5.8	20.6	21.6	58.9	19.5
60.8	21.4	17.8	62.6	10.9	26.5	23.9	49.5	26.6
59.2	32.0	8.8	68.8	13.2	18.0	24.1	49.1	26.8
60.7	13.3	26.0	63.0	7.6	29.4	24.2	41.5	34.3
58.8	4.4	36.8	59.5	6.0	34.5	24.2	41.6	34.2
50.0	35.8	14.2	61.1	13.2	25.7	24.3	34.1	41.6
49.8	11.8	38.4	53.0	7.5	39.5	24.3	34.0	41.7
49.9	19.8	30.3	53.4	11.5	35.1	23.1	26.8	50.1
49.5	30.0	20.5	56.1	12.6	31.3	21.4	19.6	59.0
39.4	44.0	16.6	55.6	12.8	31.6	17.2	12.4	70.4
38.4	53.6	8.0	65.8	13.3	20.9	13.2	9.0	77.8
39.6	17.0	43.4	47.0	11.0	42.0	0.0	2.3	97.7
39.6	25.4	35.0	46.0	13.3	40.7			
39.1	36.3	24.6	47.0	13.6	39.4			
24.5	54.2	21.3	43.5	13.1	43.4			
23.7	64.8	11.5	53.9	14.0	32.1			
25.0	5.0	70.0	39.1	11.8	49.1			
28.0	29.0	43.0	37.7	15.1	47.2			

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Chapter 10

Amines

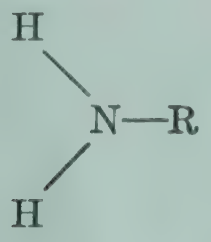
The amines have attained commercial importance only within the last two decades, although monoethanolamine, diethanolamine, and triethanolamine have been known since 1862, when they were first prepared by Wurtz. These compounds, which are ammonia derivatives with organic radicals in place of the hydrogen, appear to have all the versatility of the oxygen compounds. The resemblance of these two classes of compounds appear in the following order: the primary amines are similar to alcohols, the secondary amines to ethers, the imines to both aldehydes and oxides, and the diamines to glycols. The amines, however, are generally more hygroscopic, more soluble in water, and have lower boiling points than alcohols. Because they neutralize acids to form salts, amines are employed as corrosion inhibitors in aqueous media. This action has been studied,[1] and the inhibitory effect of a number of amines in sulfuric acid on mild steel has been tabulated.

The uses of amines have increased widely. They are used in the manufacture of new emulsifiers for cutting oils, cosmetics, insecticides, polishes, textile softeners, detergents, dyes, rubber products, pharmaceuticals, and photographic compounds. Another important use is in gas purification where the amines behave as acid neutralizers.

The large number of commercially available amines are conveniently classified into the following groups—

Alkyl amines
Ethylene amines
Alkanalamines
Arylamines

Table 10.1 gives an interesting tabulation of the boiling points of the n-alkyl primary amines and Fig. 10.1 gives the vapor pressure curves.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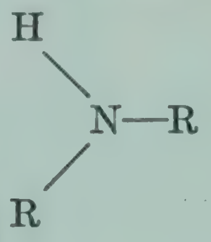
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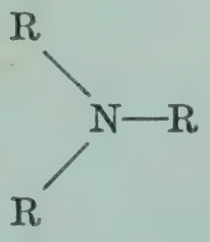
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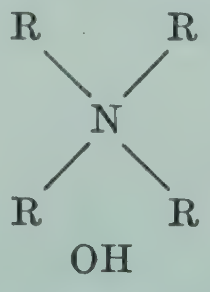
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TABLE 10.1. BOILING POINTS OF *n*-ALKYL PRIMARY AMINES

C ATOMS	BOILING POINTS, IN °C, AT FOLLOWING PRESSURE:										
	1 mm.	2 mm.	4 mm.	8 mm.	16 mm.	32 mm.	64 mm.	128 mm.	256 mm.	512 mm.	760 mm.	Calcd.
6	—	—	—	—	—	47.7	62.5	79.1	98.1	119.4	132.7	130.8
7	—	—	—	—	53.8	67.3	81.8	99.8	119.7	143.4	156.9	155.0
8	—	35.2	46.6	58.9	72.1	86.6	102.8	121.1	141.5	164.9	179.6	177.6
9	—	51.5	62.9	75.6	89.4	104.8	122.2	141.2	162.8	187.3	202.2	198.9
10	56.3	66.9	78.4	91.2	105.6	121.4	138.8	158.3	180.2	204.9	220.5	219.0
11	69.0	80.3	91.9	105.1	120.0	136.7	155.3	175.7	198.4	224.9	241.6	238.1
12	81.4	93.5	106.3	120.5	135.2	152.3	171.2	191.8	214.9	242.1	259.1	256.4
13	97.0	108.0	120.8	134.9	150.6	167.8	186.7	207.4	230.9	258.2	275.7	273.8
14	109.2	120.9	133.6	147.8	163.4	181.4	201.1	222.9	246.6	274.2	291.2	290.5
15	120.5	132.3	145.5	160.1	176.3	194.6	214.5	236.9	261.7	289.7	307.6	306.6
16	131.8	143.9	157.6	172.7	189.4	207.9	228.2	250.7	275.8	304.6	322.5	322.0
17	143.2	155.0	168.6	183.9	200.6	219.3	239.7	262.3	288.1	317.6	335.9	337.0
18	153.2	166.1	180.0	195.5	212.3	232.0	—	—	—	—	348.8[a]	351.4

[a] To avoid thermal decomposition, this boiling point was determined on a fresh sample as rapidly as possible.

Table 10.2. Solvent Properties of Amines[5]

	Ethylene Diamine	Propylene Diamine	Triethylene Tetramine	Morpholine	Morpholine Ethanol	Morpholine Ethyl Ether
Water	M	M	M	M	M	M
Alcohol	M	M	M	M	M	M
Glycols	M	M	M	M	M	M
Glycol ethers	M	M	M	M	M	M
Acetone	M	M	M	M	M	M
Methyl butyl ketone	S	S	S	M	M	M
Ethyl ether	S	S	S	M	M	M
Butyl ether	SS	S	SS	M	M	M
Naphtha	S	S	SS	S	I	M
Benzene	M	M	S	M	M	M
Turpentine	I	I	I	M	M	M
Pine oil	M	M	M	M	M	M
Paraffin oil	I	I	I	I	I	M
Castor oil	M	M	M	M	M	M
Linseed oil	I	I	I	M	S	M
Paraffin wax	SH	SH	SH	SH	SH	SS
Beeswax	I	I	SH	I	I	SS
Shellac	S	S	S	S	S	S
Rosin	S	S	S	S	SS	S
Ester gum	SS	SS	SS	S	S	S
Dammar gum	I	I	I	PS	PS	S
Copal gum	S	S	S	S	S	S
Sulfur	VS	VS	S	SS	SS	SS
Vinylite A	G	G	G	S	G	SS
Vinylite N	S	S	S	S	S	S
Vinylite 0200	G	G	G	S	G	S
Cellulose acetate	G	G	G	S	S	I
Cellulose nitrate	S	S	S	S	S	S
Benzyl cellulose	SS	SS	SS	S	S	S
Water-sol. dye	S	S	SS	I	I	I
Alcohol-sol. dye	S	S	S	S	S	S
Oil-sol. dye	S	S	S	S	S	S
Satd. brine	M	M	M	M	M	S

M = miscible in all proportions
S = sol. to over 5%
SS = sol. from 1 to 5%
PS = sol. in part
I = sol. to less than 1%
SH = sol. hot
VS = very sol.
G = gels.

The amines are solvents and plasticizers for cellulose nitrate and acetate They are used in combination with active solvents in rayon printing Bergstrom, Gilkey and Lung[3] have determined and tabulated the solubility of 288 compounds in a number of amines (Table 10.3). The properties of the amine group of solvents are presented in the following series o graphs.

(Text continued on page 411

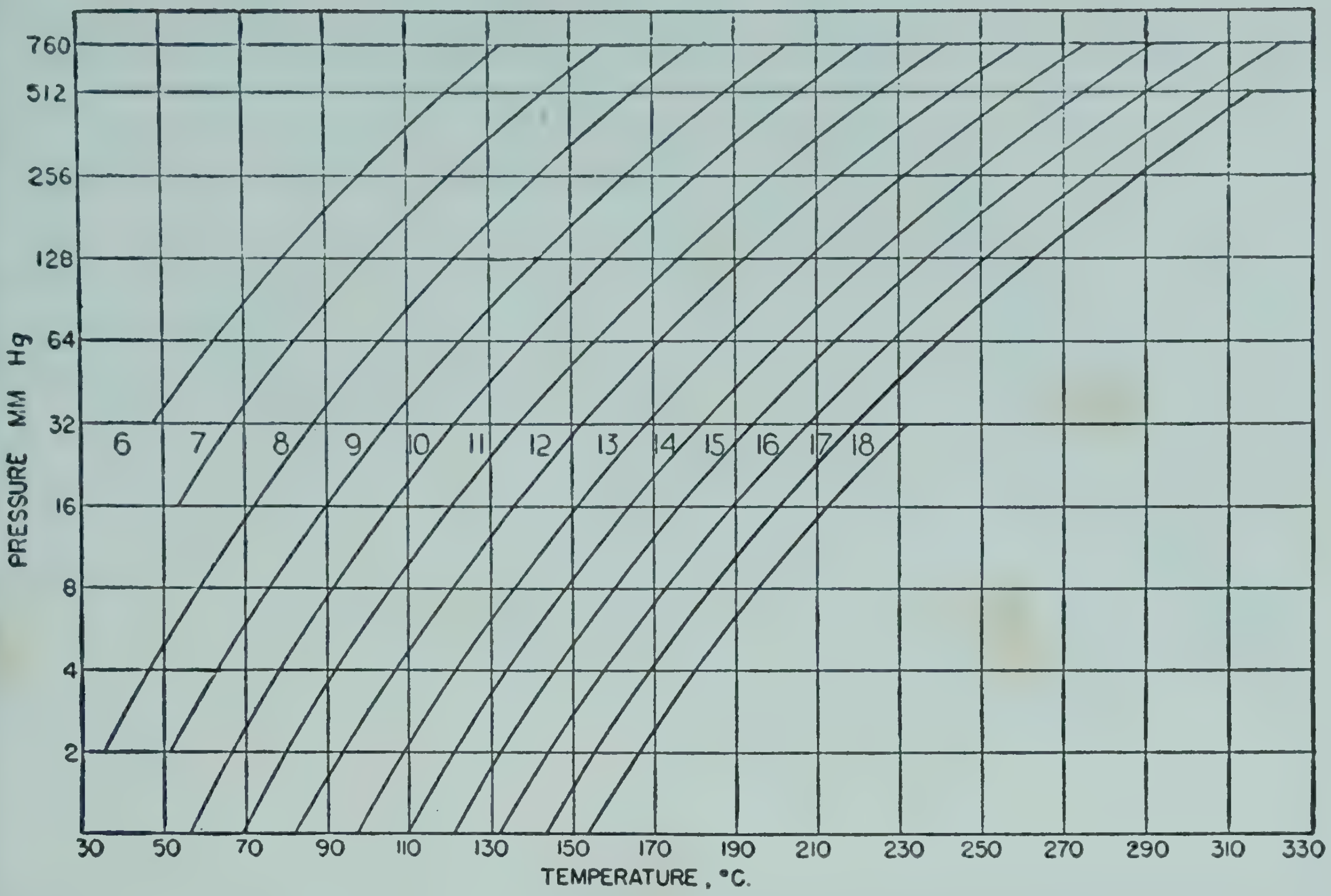


Figure 10-1. Vapor Pressure Curves of Normal Primary Aliphatic Amines. Curve numbers refer to number of carbon atoms in the molecule.[2]

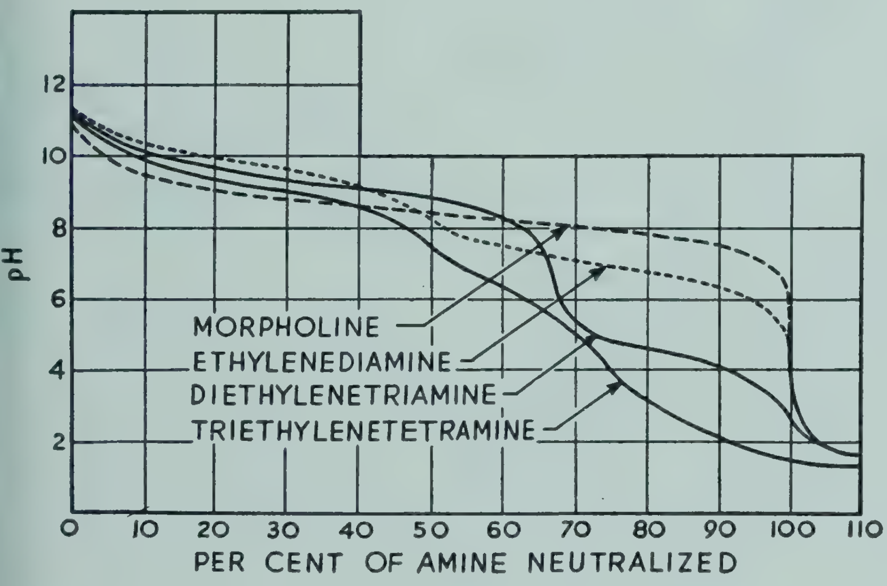


Figure 10.2. Neutralization Curves—Titrations with Hydrochloric Acid in N/2 Solutions.[4]

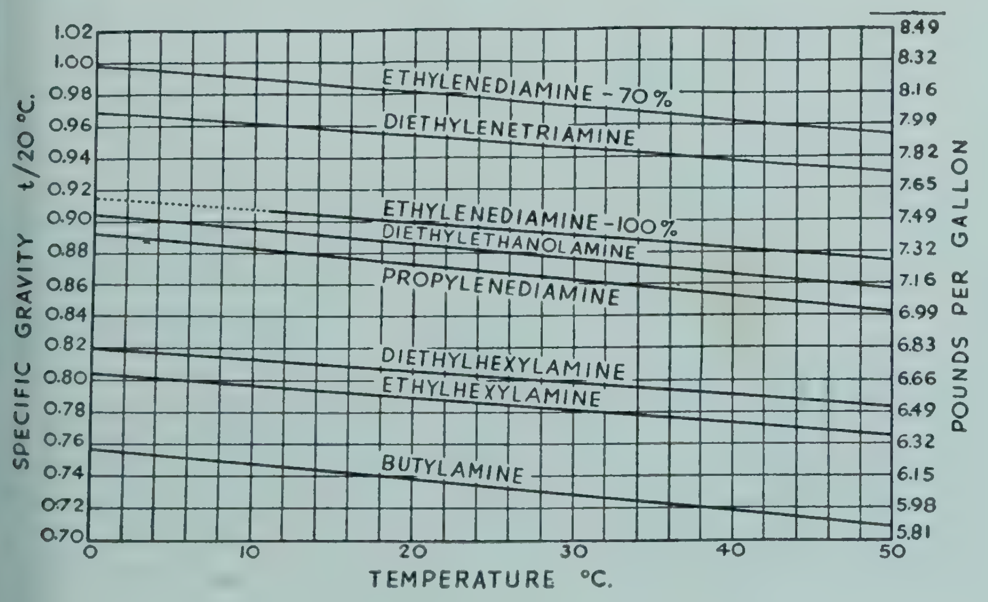


Figure 10-3. Specific Gravity and Weight per Gallon at Various Temperatures.[4]

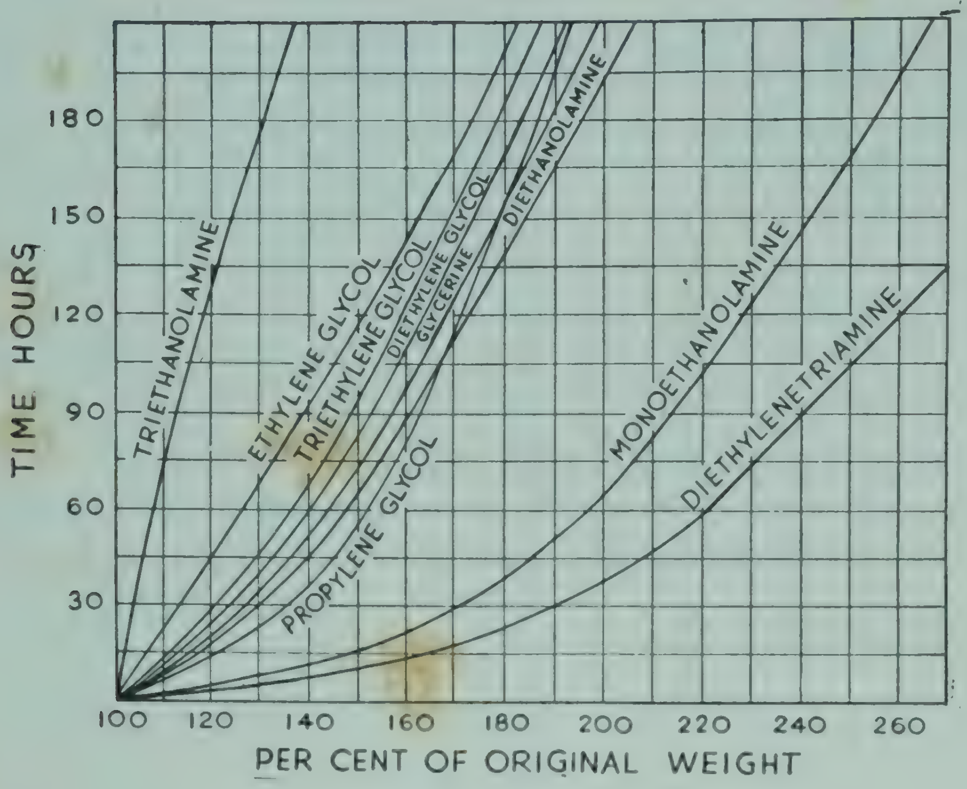


Figure 10-4. Comparative Hydroscopicities at 100 Percent Relative Humidity and 100°F.[4]

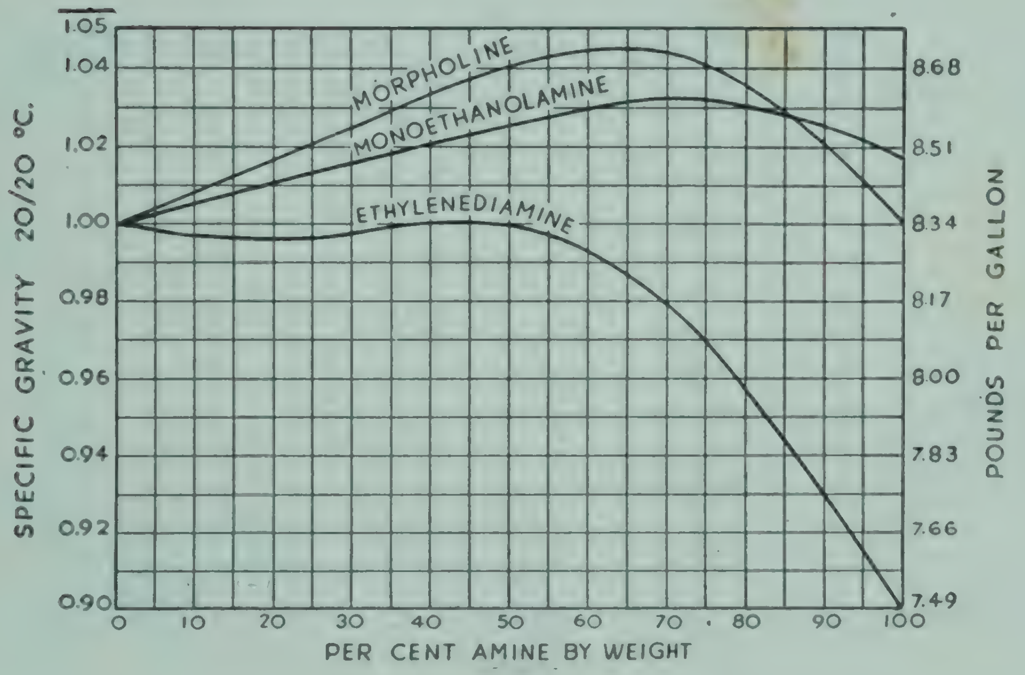


Figure 10-5. Specific Gravity and Weight per Gallon of Aqueous Amine Solutions at 20°C.[4]

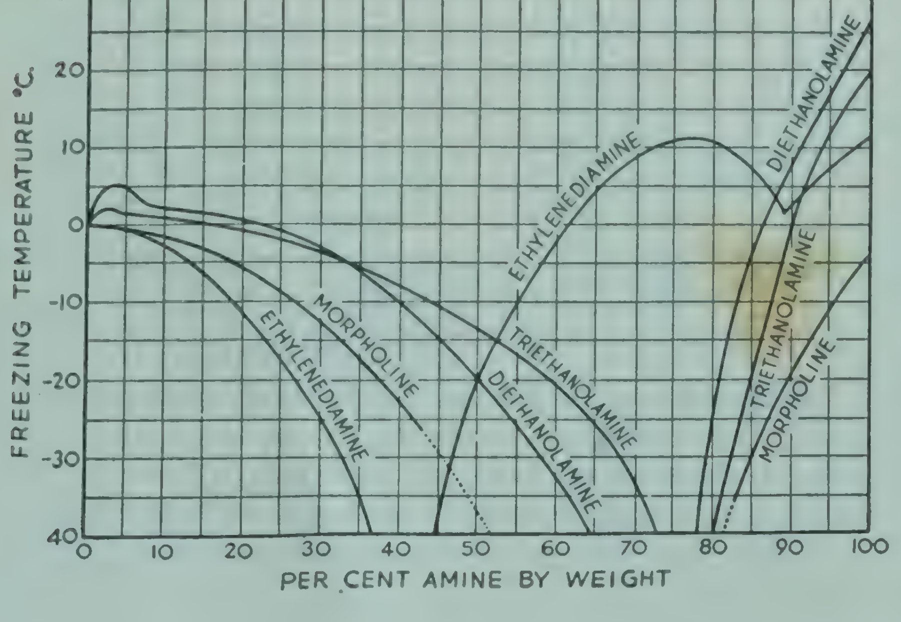


Figure 10-6. Approximate Freezing Points (Initial Crystallization) of Aqueous Amine Solutions.[4]

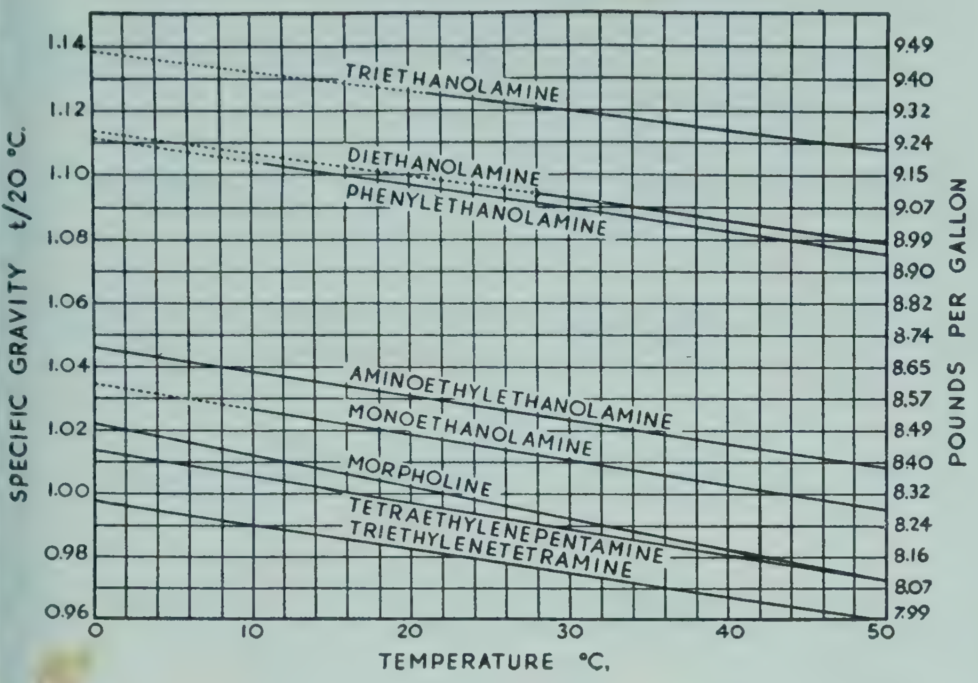


Figure 10-7. Specific Gravity and Weight Per Gallon at Various Temperatures.[4]

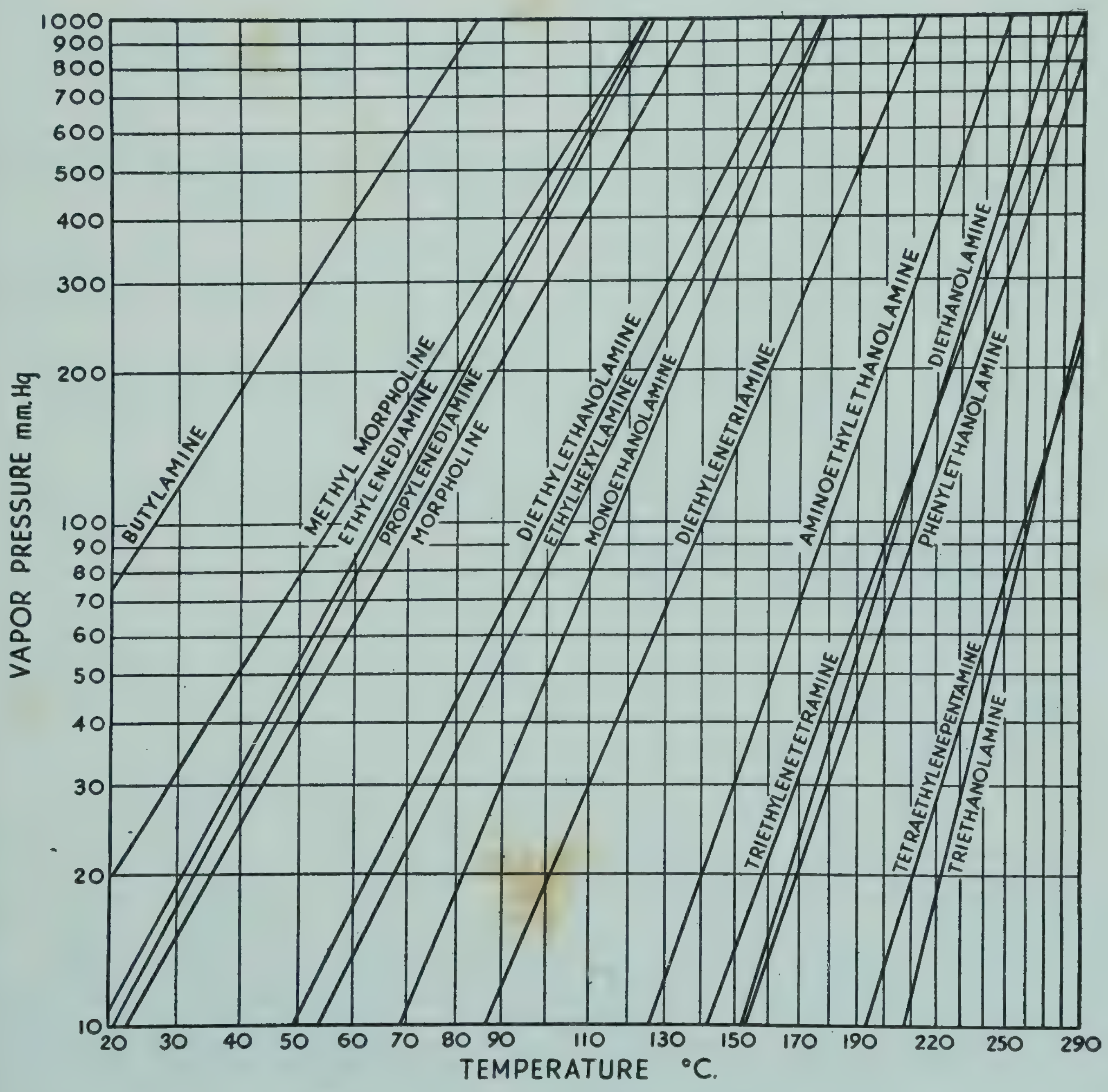


Figure 10-8. Vapor Pressures.[4]

TABLE 10-3. SOLUBILITIES OF ORGANIC COMPOUNDS IN ALIPHATIC AMINES (AT 25° + 5°C.)[8]

Abbreviation		Approx. Sol'y Range per 100 cc. of Solvent *Grams*
ins.	Insoluble or extremely slightly soluble	$(0^+$ to $10)$
ss	Slightly soluble	$(10^+$ to $40)$
s	Moderately soluble	$(40^+$ to $70)$
vs	Very soluble	$(70^+$ to $100)$
vs+	More than vs	$(100^+$ and above)
es	Extremely soluble	
misc	Miscible (in methylamine column only)	
∞	Miscible in all proportions	
n	Not soluble to an appreciably greater extent in hot solvent	
x	More soluble in heated amine, crystallizes on cooling	
m	More soluble in heated amine (in some cases because of chemical reaction)	
p	Separates into two liquid phases	
r	Solute reacts chemically with solvent. Reaction is rapid enough to be apparent. All acidic substances react more or less rapidly with amines. (The letter *r* has been omitted in these cases)	
a	Swells	
Numerals	Numerals appearing in diethylamine column indicate number of grams of solute (or of its reaction product with diethylamine) per 100 cc. of solution	

		C_2H_5OH	$\genfrac{}{}{0pt}{}{C_2H_5}{C_2H_5}>O$	CH_3NH_2	$\genfrac{}{}{0pt}{}{C_2H_5}{C_2H_5}>NH$	$(C_2H_5)_3N$	$(n\text{-}C_3H_7)_2NH$	$n\text{-}C_4H_9NH_2$	$(n\text{-}C_4H_9)_2NH$	$(n\text{-}C_4H_9)_3N$	$iso\text{-}C_5H_{11}NH_2$	$C_6H_5CH_2NH_2$	$NH_3(-33°$ C.)
1	Acenaphthene	ssx	..	..	15	sx	..	sx	s	ssx	s	s	ins
2	Acetaldehyde	..	..	misc	..	..	..	..	..	..	..	..	..
3	Acetamide	s	..	vs	ssx	ins	..	s	ins	ins	s	s	vs
4	Acetanilide	vs	ss	..	11	ssx	..	vs	ss	ssx	sx	s	..
5	Acetic acid	..	..	vs	..	.	..	..	..	..	..	..	..
6	Acetoacetic ester	∞	..	..	∞	..	..	..	∞	..	..	..	∞
7	Acetone	∞	∞	∞	..	..	..	..	..	..	..	..	..
8	Acetophenone	∞	..	..	∞	..	.	∞	..	∞	..	..	s
9	*p*-Acetophenylene diamine	..	..	..	ins	..	..	ssx	ssx	..	ssx	..	..
10	*p*-Acetotoluide	ss	s	..	ss	..	..	..	..	ssx	ssx	..	ss
11	Acetylene	s	..	s	..	..	..	..	..	..	..	..	..
12	Acetylene tetrabromide	s	∞	..	r	..	..	..	..	..	..	..	s
13	Acetylsalicylic acid	vs	ss	..	s	s	s	vs	s	ss	vs	s	..
14	Agar-agar	..	..	..	..	..	..	..	..	..	insn	..	ins
15	Alanine	ss	ins	..	..	..	..	..	..	..	insn	..	..
16	Aldol	∞	s	..	∞	..	..	∞	..	..	..	..	..
17	Alizarin	..	..	s	..	..	..	..	..	..	..	..	..
18	Allyl alcohol	∞	∞	..	∞	..	..	..	..	..	..	..	..
19	1-Aminoanthraquinone	ss	ss	..	ss	ss	ss	ssm	ss	ssx	ssm	ss	..
20	*p*-Aminobenzoic acid	s	ss	..	ins	ins	isn	ss	ins	insn	ss	ssx	..

TABLE 10-3. SOLUBILITIES OF ORGANIC COMPOUNDS IN ALIPHATIC AMINES (AT 25° ± 5°C.)—(*Continued*)[3]

		C_2H_5OH	$\substack{C_2H_5\\C_2H_5}>O$	CH_3NH_2	$\substack{C_2H_5\\C_2H_5}>NH$	$(C_2H_5)_3N$	$(n\text{-}C_3H_7)_2NH$	$n\text{-}C_4H_9NH_2$	$(n\text{-}C_4H_9)_2NH$	$(n\text{-}C_4H_9)_3N$	iso-$C_5H_{11}NH_2$	$C_6H_5CH_2NH_2$	NH_3(−33° C.)
21	*m*-Aminophenol	s	s	..	vs+	ss	..	s	s	ss	vs	s	..
22	*o*-Aminophenol	ss	ss	..	vs	ins	s	vs+	sx	ssn	s	s	vs
23	Aminosulfonic (sulfamic) acid	..	..	..	..	..	..	ssn	..	..	ssx	..	..
24	Ammonium benzoate	..	..	..	ss	..	..	vsr	..	..	vsr	..	vs
25	Ammonium citrate	..	..	..	ss	..	..	..	..	..	..	..	..
26	Amyl alcohol (iso)	∞	∞	..	∞	..	..	∞	..	..	..	∞	..
27	*n*-Amyl formate	∞	∞	∞	..	..	..	..	..	∞	..	..	..
28	Anethole	∞	∞	..	∞	..	..	..	..	..	..	..	ss
29	Anhydroformaldehydeaniline	ss	ss	..	ssn	ssx	ins	ss	ss	ssx	ssx	ssx	..
30	Aniline blue	..	..	..	ss	ins	..	ss	ins	ins	ss	ss	..
31	Anthracene	ss	ss	..	ss	ssx	..	ssx	ss	ssx	ssx	ssx	ins
32	Anthranilic acid	s	s	..	ss	ins	ssx	s	ss	ss	s	s	..
33	Anthraquinone	ss	ss	ss	..	..	..	ssx	..	..	ssx	..	ins
34	Atoxyl	..	..	..	ins	ins	..	ss	ins	ins	ss	ins	..
35	Azobenzene	ss	s	vs	vs	vsx	vs	vs	vs	s	vs	s	s
36	Azoxybenzene	s	s	..	es	..	..	..	..	..	es	..	s
37	Beeswax	..	..	..	s	s	..	s	s	ssm	s	ssm	..
38	Benzalacetophenone	ss	vs	..	vs	..	..	es	..	ssx	..	..	..
39	Benzaldehyde	∞	∞	misc	∞	..	..	..	..	..	..	..	es
40	Benzamide	s	vss	..	ss	ins	s	s	ss	ins	s	s	vs
41	Benzene	∞	∞	..	∞	..	..	∞	∞	∞	..	∞	s
42	Benzidine	s	ss	..	ss	ss	..	s	ssx	ins	sx	s	..
43	Benzil	vs	vs	vs	vs	ss	sx	es	ss	ss	es	es	s
44	Benzoic acid	vs	vs	vs	ssx	ssx	..	vs	s	ssp	s	sx	vs+
45	Benzoic sulfinide (Saccharin)	ss	ins	r	..	..	..	..	..	..	ss	..	..
46	Benzoin	s	..	..	..	..	..	vs	..	..	..	..	..
47	Benzophenone	s	s	vs	es	es	..	es	vs+	sx	es	es	s
48	Benzyl acetate	∞	∞	..	∞	..	..	..	∞	..	..	∞	s
49	Benzyl alcohol	∞	∞	..	∞	..	..	..	..	∞	..	..	∞
50	Borneol	vs	vs	..	es	..	..	..	..	..	..	..	s
51	*o*-Bromoacetanilide	..	..	vs	..	..	..	..	..	..	..	..	..
52	*p*-Bromoaniline	vs	vs	..	esx	vs+	esx	vs+	vs	ssx	vs	vs+	..
53	Bromcamphor	s	vs	..	vs+x	s	..	vs+x	vs+	ssx	vs	vs	..
54	Bromocresol green	..	..	..	ss	ins	..	s	ssn	ins	s	s	..
55	1-Bromonaphthalene	∞	∞	..	∞	..	..	..	..	∞	..	..	..
56	*p*-Bromonitrobenzene	s	s	..	s	..	..	..	..	..	..	..	..
57	*o*-Bromotoluene	s	..	..	∞	..	..	..	∞	∞	..	∞	..
58	*p*-Bromotoluene	s	s	..	es	..	..	..	es	..	..	..	..
59	*n*-Butyl alcohol	∞	..	..	∞	..	..	..	..	..	∞	∞	∞
60	tert-Butyl alcohol	..	..	∞	..	..	..	..	..	..	..	..	..

TABLE 10-3. SOLUBILITIES OF ORGANIC COMPOUNDS IN ALIPHATIC AMINES (AT 25° ± 5°C.)—(*Continued*)[3]

61	*n*-Butyl xyanide	∞	s	..	∞	..	..	∞	..	..	∞	..	s
62	*n*-Butyl ether	∞	∞	..	∞	..	..	∞	∞	∞	∞	..	..
63	*n*-Butyl formate	∞	∞	..	∞	..	..	..	∞	..	..	..	..
64	*n*-Butyl stearate	..	..	..	∞	..	..	∞	∞	∞	∞	rss	..
65	Caffeine	ss	ss	..	ss	..	..	ssx	..	..	ssx	..	ss
66	Calcium acetate	ins	..	..	insn	..	..	..	..	..	..	..	..
67	*n*-Calcium butyrate	..	..	..	..	..	..	insn	..	..	..	..	..
68	Calcium formate	ins	..	..	..	..	..	..	..	..	insn	..	..
69	*d*-Camphor	es	vs	..	es	es	..	es	vs	vsx	es	es	vs
70	Carbon disulfide	∞	∞	..	r	..	..	esr	..	∞	..	..	r
71	Casein	..	..	..	ins	ins	..	ins	ins	ins	ins	ins	..
72	Cellulose	ins	ins	..	ins	ins	..	ins	ins	ins	ins	insa	ins
73	Cellulose acetate	..	..	..	ss	ins	ins	es	ins	ins	s	s	es
74	Cellulose nitrate	..	..	..	s	ins	..	vs	ss	ins	vs	vs	s
75	Cerulein	..	..	vs	..	..	..	..	..	..	..	..	..
76	Cetyl alcohol	s	s	vsx	..	..	..	es	..	s	..	..	ins
77	Chloroacetic acid (mono)	s	s	..	srx	vsxp	..	sx	ssxr	ssp	vs	ssrm	vs
78	*p*-Chlorodiphenyl	s	s	..	vs+	vs+x	..	vs	vs	sx	vs	vs	..
79	Chloroform	∞	∞	∞ r	∞	..	..	..	..	..	..	..	sr
80	Cholesterol	ssx	s	..	..	..	vs+	..	..	..	vs+	..	ins
81	Chromotropic salt	..	..	..	..	..	..	insn	..	..	..	..	..
82	Cinchonine	ss	ss	..	..	..	..	ssn	..	..	ssx	..	ins
83	Cinnamic acid	s	vs	..	s	ss	..	sx	ss	ssx	s	ssx	s
84	Coconut oil	..	..	..	∞	∞	..	∞	∞	∞	∞	∞	..
85	Copal	..	..	..	..	..	..	..	..	..	insn	..	ss
86	Crystal violet	..	..	..	ins	ins	..	vs	ins	ins	s	s	s
87	Cyclohexanol	s	s	..	∞	..	..	..	..	..	..	..	..
88	*o*-Dianisidine (bianisidine)	s	vs	..	ss	ins	..	sx	ss	ins	s	s	..
89	Diazoaminobenzene	s	vs	..	vs	..	..	..	..	..	es	..	vs
90	*p*-Dibromobenzene	s	..	..	40	vs+x	..	vsx	vs	sx	vs	vs+	ss
91	2,3-Dibromopropyl alcohol	vs	∞	..	..	..	..	..	..	..	..	..	..
92	Dichloramine-T	..	..	..	vsr	sr	..	vsr	ssr	r	vsr	vs+r	r
93	*p*-Dichlorobenzene	es	vs	..	53	esx	..	es	ves	vs+x	esx	es	ss
94	Dichlorogallein	..	..	s	..	..	..	..	..	..	..	..	s
95	Dichlorohydrin	∞	∞	..	∞	..	..	..	..	..	..	..	..
96	2,3-Dihydroxyquinoxaline	..	..	..	..	..	..	insn	..	..	..	..	s
97	Dimethyalminoazobenzene	x	..	..	sx	ssx	ssx	sx	s	ss	s	s	..
98	*p*-Dimethylaminobenzaldehyde	s	s	..	..	..	..	sx	..	..	..	..	..
99	Dimethylaniline	s	∞	..	∞	..	..	..	..	..	..	..	ss
100	Dimethylethylcarbinol	s	s	..	∞	..	..	..	∞	..	∞	∞	..
101	Dimethylglyoxime	vs	vs	..	ssx	s	ssx	vs	ss	ssx	vs	s	..
102	2,6-Dimethylquinoline	vs	vs	..	vs	..	..	..	..	..	..	..	..
103	2,2-Dinaphthylamine	ss	..	..	ssx	ssx	ssx	sx	ssx	ssx	s	ss	..
104	2,4-Dinitroaniline	ss	..	vs	..	..	..	..	..	..	..	..	..
105	*m*-Dinitrobenzene	ssx	..	vs	9.3	ss	..	s	ss	ssx	s	s	..
106	3,5-Dinitrobenzoic acid	vs	ss	..	ss	ss	ssx	s	ss	ssx	vs	sm	..
107	4,4′-Dinitrodiphenyl	ss	vs	..	ss	ss	..	ssx	ssx	ssx	ssx	ssx	..
108	2,4-Dinitro-1-naphthol-7-sulfonic acid	..	..	..	ss	..	..	..	..	..	..	..	..
109	2,4-Dinitrophenol	ss	vs	..	ss	..	..	sx	..	ssn	vs	..	vs

TABLE 10-3. SOLUBILITIES OF ORGANIC COMPOUNDS IN ALIPHATIC AMINES (AT 25° ± 5°C.)—(*Continued*)[3]

		C_2H_5OH	$\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\!>\!O$	CH_3NH_2	$\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\!>\!NH$	$(C_2H_5)_3N$	$(n\text{-}C_3H_7)_2NH$	$n\text{-}C_4H_9NH_2$	$(n\text{-}C_4H_9)_2NH$	$(n\text{-}C_4H_9)_3N$	$\text{iso-}C_5H_{11}NH_2$	$C_6H_5CH_2NH_2$	$NH_3(-33°\ C.)$
111	Diphenyl	ss	s	..	41	s	..	vs	s	sx	vs	vs	ss
112	Diphenylamine	vs	vs	..	es	vs	es	es	vs	sx	es	es	..
113	Diphenylbenzamide	..	..	..	ss	..	..	..	..	..	ssx	..	..
114	Diphenylguanidine	..	..	..	ss	ins	..	vs	s	ssx	vs	s	..
115	Diphenyl ketoxime	..	..	vs	..	..	..	..	..	..	..	..	..
116	Diphenyl sulfone (phenyl sulfone)	ss	s	..	ssx	ssx	..	ssx	ss	ssx	ssx	sx	..
117	Diphenylurea (sym.)	s	s	..	ss	ins	..	ss	ss	ssx	s	ssx	s
118	4,4′-Dipyridyl (bipyridine)	vs	..	..	..	..	..	vsx	..	..	sx	..	vs
119	Di-*p*-tolylselenide	..	..	..	..	..	..	es	..	..	..	..	..
120	Eosin	s	..	..	ss	ins	..	vs	ss	ins	vs	s	s
121	Ethyl alcohol	∞	∞	..	..	..	..	..	∞	..	..	∞	..
122	Ethyl carbonate	s	..	..	ssr	..	..	∞	..	..	..	∞	sr
123	Ethyl cyanoacetate	∞	∞	..	∞	..	..	..	..	..	..	..	..
124	Ethylene dibromide	s	∞	spr	∞	..	..	..	∞	..	..	∞	..
125	Ethylene glycol	∞	ss	..	∞	..	∞	..	..	..	∞	..	..
126	Ethyl iodide	s	s	..	∞	..	..	..	..	∞	..	esr	s
127	Ethyl malonate	∞	∞	..	∞	..	..	..	∞	..	∞	..	..
128	Ethyl oxalate	s	..	..	∞	..	..	..	∞	..	..	ssr	..
129	Ethyl sulfate	..	..	..	r	..	..	..	rs	..	..	..	..
130	Fluorene	ss	vs	..	13	ssx	sx	s	s	ssx	s	s	ins
131	Fluorescein	vs	ss	..	ss	ins	..	s	ins	ins	s	s	s
132	Galactose	ss	..	vs	..	..	..	..	..	..	..	..	..
133	Gallein	..	..	ss	..	..	..	..	..	..	..	..	..
134	Gallic acid	s	ss	..	insn	insn	..	s	insx	insn	s	ssm	s
135	Gelatin	..	..	..	ins	ins	..	insn	ins	ins	ins	ins	..
136	Glucose	ss	ins	vs	ss	ins	ssn	vs+	ins	ins	s	s	vs
137	β-Glucose pentaacetate	ss	ss	..	..	..	..	es	..	..	..	..	..
138	Glycerol	∞	ins	vs	..	..	..	..	..	..	..	..	..
139	Guaiacol	∞	∞	..	∞	..	..	..	..	..	..	..	..
140	Guanidine nitrate	..	..	..	ss	..	..	..	..	..	..	..	vs
141	Gum arabic	..	..	..	insn	ins	..	ins	ins	ins	ssn	ss?	..
142	H acid	ss	ss	..	..	..	..	insn	..	..	..	..	..
143	Hemoglobin	..	..	..	ins	..	..	insn	..	..	..	..	ss
144	Hexaethylbenzene	s	vs	..	..	..	..	ssx	..	..	ssx	..	..
145	Hexamethylenetetramine	ss	ins	..	ssn	..	..	ssn	..	..	..	..	..
146	Hippuric acid	ss	vss	vs	ssx	..	..	..	..	..	vs	..	vs
147	Hydrazine sulfate	ins	..	..	ins	..	..	..	..	..	..	..	insr
148	Hydroquinone	vs	vs	vs	35	ss	s	s	s	ss	s	ssx	vs
149	Hydroxylamine hydrochloride	s	ins	vs	..	..	..	..	..	..	..	..	..
150	Indigotin	ins	ins	vs	ins	ins	..	ss	ss	ss	ins	ss	ss

TABLE 10-3. SOLUBILITIES OF ORGANIC COMPOUNDS IN ALIPHATIC AMINES (AT 25° ± 5°C.)—(*Continued*)[3]

151	Indole	vs	vs	..	es	..	..	es	..	..	..	..	vs
152	Isatin	s	ss	..	..	..	..	vs	..	..	..	..	s
153	Isoquinoline	∞	∞	..	∞	..	..	..	∞	..	∞	..	s
154	Lactose	ss	ins	..	ss	ss	..	ss	ins	ins	es	ins	vs
155	Lanolin	..	..	..	es	es	..	es	es	es	es	es	..
156	Linseed oil, raw	..	..	..	∞	∞	..	∞	∞	∞	∞	∞	..
157	Lysol	..	..	..	∞	..	..	..	..	..	..	..	..
158	Maleic acid	s	ss	..	ins	ins	..	ssn	ins	ins	sex	insm	..
159	Malic acid	vs	ss	..	ins	ins	ins	ssn	ins	ins	ssn	ssx	ss
160	Malonic acid	s	ss	..	ins	insn	insx	ss	ins	ss?	ss	ins	ins
161	Mannite	ss	ins	..	ss	ins	..	ss	ins	ins	ssn	ins	ss
162	*d*-Menthol	vs	vs	..	es	es	es	es	es	es	es	es	es
163	Mercuric acetate	ss	..	..	insr	ins	s	vs	ss	ins	ss	ins	s
164	Mercuric cyanide	s	..	vs	..	..	..	es	..	ssn	..	..	vs
165	Mercury diphenyl	ss	..	..	ss	ins	ss	ss	ss	ins	ss	ins	..
166	Mercury di-*p*-tolyl	..	..	..	..	..	..	ssx	..	ssx	ssx	..	..
167	Methanol	∞	∞	∞	..	..	..	∞	..	∞	..	..	..
168	*meso*-Methyl acridine	vs	vs	..	..	..	..	..	..	..	es	..	..
169	Methylene aminoacetonitrile	..	..	..	ss	ss	...	ss	ins	ssx	ss	ins	..
170	Methylene dianiline	..	..	..	insn	ss	..	ss	ss	insx	ss	ss	..
171	Methyl orange	ss	ins	ss	ins	ins	ins	ssn	ins	ins	ss	ss	..
172	Mucic acid	ins	..	..	ins	ins	insn	ss	ins	ins	ss	ins	s
173	Naphthalene	ss	vs	..	27	sx	..	vsx	s	sx	vs	sx	ss
174	Naphthionic acid	ss	ins	..	ss	ins	..	s	ins	ins	s	ss	..
175	1-Naphthol	vs	vs	vs	..	..	..	..	..	..	..	..	..
176	2-Naphthol	vs	vs	vs	es	vs+	..	es	es	vs	es	es	ss
177	Naphthol yellow	..	..	..	ins	ins	..	ss	ins	ins	ins	ins	..
178	Night blue	..	..	..	s	s	..	s	s	s	s	s	..
179	*p*-Nitroacetanilide	s	ss	..	ss	..	..	..	..	..	..	..	..
180	*m*-Nitroaniline	s	ss	..	sx	ssx	..	s	ss	ssx	s	s	s
181	*p*-Nitroaniline red	..	..	..	ss	ss	..	s	ssx	ssx	s	s	..
182	*m*-Nitrobenzaldehyde	vs	vs	vs	..	..	..	..	..	..	..	..	..
183	Nitrobenzene	∞	∞	∞	..	..	..	∞	..	∞	..	..	vs
184	*m*-Nitrobenzenesulfonamide	..	..	vs	..	..	..	..	..	..	..	..	..
185	*o*-Nitrobenzoic acid	s	s	vs	..	..	..	..	..	..	..	..	..
186	*p*-Nitrobenzoic acid	ss	ss	..	ssx	insn	ssx	vsx	ss	ss	s	sx	ss
187	*p*-Nitrobromobenzene	ss	..	..	ss	ss	ssx	sx	ss	ssx	s	sx	..
188	*o*-Nitrophenol	vs	vs	vs	..	..	..	..	..	..	..	..	..
189	*p*-Nitrophenol	vs	s	..	13	ss	ssx	vs	ss	ssm	vs	s	s
190	*p*-Nitrophenylhydrazine	..	..	..	..	..	..	vs	..	ssx	..	..	..
191	*o*-Nitrotoluene	∞	∞	vs	..	..	..	..	...	..	..	..	..
192	*p*-Nitrotoluene	s	s	..	vs+x	..	..	..	..	sx	vsx	..	..
193	3-Nitro-4-toluidine	vs	..	..	sx	..	..	vsx	..	ssx	..	..	s
194	Nitrourea	vs	vs	..	ins	..	..	..	..	..	..	..	vs
195	Oleic acid	∞	∞	..	∞	∞	..	∞	∞	∞	∞	∞	ins
196	Olive oil	..	..	..	∞	∞	..	∞	∞	∞	∞	∞	..
197	Orange IV	..	..	..	ss	ins	..	ss	ss	ins	ssn	ss	..
198	Oxalic acid.2H_2O	s	ss	..	ins	ins	..	insn	insn	ins	ins	ins	ins
199	Oxanilide	ss	ss	..	0.5	..	..	..	..	..	..	..	..

TABLE 10-3. SOLUBILITIES OF ORGANIC COMPOUNDS IN ALIPHATIC AMINES (AT 25° ± 5°C.)—(*Continued*)[3]

		C_2H_5OH	$\begin{matrix}C_2H_5\\C_2H_5\end{matrix}>O$	CH_3NH_2	$\begin{matrix}C_2H_5\\C_2H_5\end{matrix}>NH$	$(C_2H_5)_3N$	$(n\text{-}C_3H_7)_2NH$	$n\text{-}C_4H_9NH_2$	$(n\text{-}C_4H_9)_2NH$	$(n\text{-}C_4H_9)_3N$	iso-$C_5H_{11}NH_2$	$C_6H_5CH_2NH_2$	$NH_3(-33°\ C.)$
201	Paraffin	..	..	..	ss	sx	..	s	sm	sx	s	ssx	ins
202	Paraffin oil	..	..	..	∞	..	..	∞	..	∞	..	..	..
203	*n*-Pentane	∞	..	∞	..	..	..	..	..	..	..	..	..
204	2-Pentene	..	..	..	∞	..	..	..	..	..	..	..	..
205	Penacetin	ss	ss	..	ss	ins	ssx	s	ss	ssx	s	ss	..
206	Phenanthrene	ss	s	..	s	..	..	..	..	..	..	vs	ins
207	Phenol	∞	∞	vs	es	..	..	..	..	..	es	..	vs
208	Phenolphthalein	s	ss	vs	s	ss	..	s	ss	ss	s	s	..
209	Phenylacetic acid	es	vs	vs	..	..	..	vsx	..	..	..	..	..
210	*meso*-Phenyl acridine	ss	s	..	..	..	..	..	..	..	ssx	..	..
211	Phenylazo-1-naphthylamine	..	..	..	..	..	..	..	..	ssx	s	..	..
212	*o*-Phenylenediamine	vs	vs	..	..	..	..	sx	..	..	sx	..	vs
213	Phenylglucosazone	ss	..	..	..	..	..	sx	..	..	vs	..	vs
214	Phenylhydrazine	∞	∞	∞	..	..	..	..	..	..	..	..	..
215	Phenylmercuric bromide	..	..	..	..	..	..	ssx	..	..	ssx	..	..
216	2-Phenylquinoline	vs	vs	..	vs	..	..	vs	..	..	s	..	..
217	Phenyl-*p*-tolyl sulfone	..	..	..	6.3	ins	ins	ss	ss	ssx	ssx	ss	..
218	Phenyl urea	vs	vs	..	ss	ss	ssn	s	ss	ssx	vs	s	s
219	Phthalic acid	s	ss	ins	ins	ins	..	ins	ins	insx	..	ssx	ins
220	Phthalic anhydride	s	ss	ins	sm	ss	..	s	ss	ins	s	ssm	..
221	Phthalimide	s	ss	..	s	ss	ss	s	sx	ssm	s	s	vs
222	Picric acid	s	ss	vs	ssp	ss	vs	vs+	s	ssx	vs	s	es
223	Potassium amide	r	ins	..	ins	..	..	insn	..	..	..	..	vs
224	Potassium ethyl sulfate	..	..	..	ins	..	..	..	..	..	..	..	vs
225	Potassium quinaldine	r	vs	..	..	..	..	vs	..	..	..	..	es
226	Potassium triphenylmethyl	r	s	..	..	..	..	s	..	..	..	..	..
227	Pyridine	∞	∞	∞	..	..	..	..	..	..	..	..	∞
228	Pyrogallol	vs+	vs+	vs	ssm	ss	..	s	s	ss	s	sm	es
229	Pyrrole	vs	vs	..	∞	..	..	..	..	..	..	..	..
230	Quinaldine	vs	vs	..	∞	..	..	∞	..	∞	∞	..	s
231	Quinaldine picrate	ss	..	..	es	..	..	es	vsx	ss	..	..	..
232	Quinine	es	vs+	..	s	ssm	s	vs	ssm	ss	vs	s	insol
233	Quinoline	s	..	..	∞	..	..	∞	∞	∞	..	∞	∞
234	Quinoline methiodide	..	..	..	..	..	..	vsx	..	..	vs	..	vs
235	Quinoline yellow (water soluble)	..	..	..	ins	ins	..	ss	ss	ins	ssn	ss	..
236	Quinone	vs	vs	sr	vsr	..	..	..	..	..	..	..	..
237	Resorcinol	es	vs	vs	s	..	..	vs	..	..	..	..	es
238	Rosaniline	s	ins	vs	ins	ins	..	ss	ins	ins	ss	ss	s
239	Rosin	vs	vs	..	s	s	..	vs	vs	ins	s	s	insr
240	Rosolic acid	ss	s	..	ss	ss	..	s	ss	ss	s	s	ss

TABLE 10-3. SOLUBILITIES OF ORGANIC COMPOUNDS IN ALIPHATIC AMINES (AT 25° ± 5°C.)—(*Continued*)[3]

241	Rubber, vulcanized	ins	ins	..	a	a	..	a	a	a	a	ins	ins
242	Salicylic acid	vs	vs	..	vs	sp	sx	vs+	ss	ssm	es	s	..
243	Selenium	ins	ins	..	ins	ins	..	ins	ins	ins	ins	ins	ins
244	Shellac, white	..	..	..	ins	ins	..	ins	ins	ins	insn	ins	..
245	Skatole	s	..	..	es	..	..	..	..	es	..	..	s
246	Soap	..	..	..	..	..	..	ins	..	..	ins	..	ins
247	Sodium alizarin sulfonate	..	..	..	ss	ins	..	s	ss	ins	s	s	ins
248	Sodium benzoate	ss	..	..	insn	..	..	insn	..	..	..	..	..
249	Sodium indigo sulfonate	..	..	..	ins	ins	..	ss	ins	ins	ss	ss	..
250	Sodium-*p*-nitrophenylantidiazotate	..	..	..	..	..	..	vs	..	..	..	..	s
251	Starch (corn)	ins	ins	..	ins	ins	..	ins	ins	ins	ins	ins	insa
252	Stearic acid, tech.	ss	s	..	es	vs+	es	es	vs+	vs	vs	ssx	ins
253	Strychnine	ins	ins	..	..	..	..	ss	..	..	..	..	..
254	Succinic acid	s	ss	ins	insn	ss	ssx	ins	ins	ins	ins	ssx	..
255	Succinimide	s	..	..	ss	ins	s	vsx	ss	ssx	sx	ss	..
256	Sucrose	ss	..	vs	ss	ss	..	vs	ins	ins	s	vs	vs
257	Sulfanilic acid	ss	ss	..	ssn	ss	..	s	ss	ss	s	ss	vs
258	Sulfonal	ss	ss	..	..	..	..	ssx	..	..	ssx	..	s
259	Sulfur, rhombic	ins	ins	..	s	s	..	vs	ss	ssx	s	s	s
260	Tallow	..	..	..	vsx	..	..	..	..	..	es	..	..
261	Tannic acid	ss	ss	..	ss	ins	insn	ss	ins	ins	ss	ss	ss
262	Tartaric acid	s	ss	ins	ins	ins	..	ss	ss	insn	ss	ssx	ins
263	Tetraethylammonium iodide	..	..	..	ins	ins	..	ins	ins	insn	ins	ins	ss
264	Tetraethyl lead	∞	∞	..	∞	..	..	∞	..	..	..	..	..
265	Tetrahydronaphthalene	vs	vs	..	∞	..	..	∞	..	∞	..	..	..
266	Tetramethyldiaminobenzophenone	vs	vs	..	0.6	ss	ssx	ss	ss	ssx	ssx	ssx	ss
267	Tetraphenyl lead	..	..	..	..	..	..	ssx	..	..	ssx	..	..
268	Tetraphenylmethane	..	..	..	ss	ss	ss	ssx	ssx	ssx	ssx	ssx	ss
269	Thymol	vs	vs	vs	es	es	es	es	es	vs	es	es	vs
270	*o*-Tolidine	vs	..	..	s	ss	ssx	s	ss	ssx	s	s	vs
271	Toluene	∞	∞	∞	..	..	..	..	..	∞	..	..	..
272	*p*-Toluenesulfonamide	..	..	..	vs	ss	vs	vs+	s	ssx	vs	s	s
273	*p*-Toluidine	s	s	..	es	vs+	..	es	vs+	sx	es	es	vs
274	Trichlorogallein	..	..	ss	..	..	..	..	..	..	..	..	..
275	2,4,6-Trinitroaniline	ins	..	es	..	..	..	..	..	..	..	..	..
276	1,3,5-Trinitrobenzene	ss	vs	..	es	ss	sp	s	ss	ss	s	s	vs
277	2,4,6-Trinitrotoluene	ss	vs	..	s	ss	sp	vs	ss	ss	s	s	s
278	Triphenylmethane	ss	vs	..	25	s	sx	s	s	ss	s	s	..
279	Triphenylselenonium iodide	..	..	..	..	..	..	ssn	..	..	ssn	..	..
280	Tyrosine	ins	ins	..	ss	ins	ins	ss	ins	ins	ss	ins	..
281	Urea	ss	ss	vs	ins	ins	..	ss	ins	ins	ss	ss	s
282	Uric acid	ins	ins	ins	..	..	..	..	..	insn	insn	..	ins
283	Wax, carnauba	..	..	..	ss	..	..	..	..	..	..	..	..
224	Wax, Japan	..	..	..	vs	..	..	..	..	..	..	..	..
285	*m*-Xylene	vs	vs	∞	..	..	..	..	..	..	..	..	..
286	1,3,5-Xylenol	s	..	..	es	vs+	..	es	vs	vs	es	es	..
287	Xylose (crude)	ins	ins	..	es	..	..	s+	..	..	s	..	..
288	Zinc stearate	..	..	..	ss	ins	ss	vs?	ss	ins	s?	s	..

ALKYLAMINES

Monomethylamine (CH_3NH_2). Monomethylamine is a colorless, flammable gas with a strong ammoniacal odor; it is sold commercially as a 30 per cent by weight aqueous solution. It is soluble in ethyl alcohol, ethyl ether, and many other organic substances, as well as water. It is used in the tanning industry, in the manufacture of dyestuffs, in many synthetic products, and in the treatment of cellulose acetate rayon for dyeing.

Typical Properties and Specifications

Boiling point (75 mm)	−6°C
Flash point (30% solution)	0.3°C
Melting point	−92.5°C
Specific gravity at −10.8°/15°C	0.699
Solubility in water	Very soluble
Weight per gallon (30% solution) at 68°F	7.7 lbs.
Ammonia	Less than 0.2% by wt. of solution
Concentration	3 to 3.5% by wt. in water gas
Formaldehyde	Less than 0.3% by wt. of solution
Purity	Not less than 98 mol % of total amines

Dimethylamine [$(CH_3)_2NH$]. Dimethylamine is a colorless gas with a strong ammoniacal odor. The commercial product is an aqueous solution containing 25 per cent by weight of dimethylamine. It is soluble in ethyl alcohol, ethyl ether, water, and many organic solvents. It is used as a dehairing agent in the tanning industry, in the manufacture of antioxidants, dyes, flotation agents, gasoline stabilizers, pharmaceuticals, rubber accelerators, emulsifiers, and cleaning compounds.

Typical Properties and Specifications

Boiling point (764 mm)	7.2 to 7.3°C
Description	Gas at ordinary temperature
Flash point (25% solution)	Approx 6.25°C
Melting point	−96°C
Specific gravity at −6°C	0.6865
Solubility in water	Soluble
Weight per gallon (25% solution) (68°F)	Approx. 7.8 lbs.
Ammonia	Not more than 1% by wt. of sol.
Concentration	25 to 25.5% by weight in water
Formaldehyde	Not more than 0.5% by wt. of sol.
Purity	Not less than 98 mol. % of total amines

Trimethylamine [$(CH_3)_3N$]. Trimethylamine is a colorless, flammable, easily condensible gas with a pungent, ammoniacal odor. The commercial product is an aqueous solution containing 25 per cent by weight of trimethylamine. It is very soluble in water and is used as a warning agent in bottled gas, as an insect attractant, and in organic synthesis.

Typical Properties and Specifications

Boiling point	Approx. 3.5°C
Critical temperature	161°C
Critical Pressure	41 atm
Decomposition temperature	800–1300°C
Dielectric constant at 4°C	2.9
Electrical conductivity	2.2×10^{-12} reciprical ohms at −33.5°C
Heat of combustion	578.6 kg. cal. per mol
Ionization constant at 25°C	6.5×10^{-5} for solutions 0.001 *N* to 0.06 *N*
Heat of evaporization at B. P.	95.6 cal. per g.
Melting point	−124°C
Specific gravity at −5°C	0.662
Surface tension at −4°C	17.4 dynes per cm.
Solubility in water at 19°C.	1 liter of aqueous saturated sol. contains 410 g. of amine
Absolute viscosity at −33.5°C	3.208 millipoises
Ammonia	Not more than 0.2% by wt. of solution
Formaldehyde	Not more than 0.3% by wt. of solution
Purity	Not less than 98 mol %

Monoethylamine ($C_2H_5NH_2$). Monoethylamine is a water-white liquid which is commercially available as a 70% aqueous solution. It is soluble in ethyl alcohol, methyl alcohol, the paraffin hydrocarbons, aromatic and aliphatic hydrocarbons, ethyl ether, ethyl acetate, acetone, fixed oils, mineral oil, oleic and stearic acids. It is also soluble in hot paraffin and carnauba waxes, which solidify when cooled.

Typical Properties and Specifications
(Anhydrous grade)

Distillation range	15–18°C
Flash point (open cup)	Below 20°F
Purity	97–99%
Specific gravity at 15/15°C	0.689
Weight per gallon	5.70 lbs
(70% Solution)	
Boiling point	16.6°C
Color	Water-white
Critical temperature	183.2°C
Dissociation constant at 25°C.	5.6×10^{-4}
Heat of combustion	Gas 9157 cal./g. Liquid 9058 cal./g.
Heat of vaporization at 15°C	14.57 cal./g.
Heat of solution in water at 19°C	6330 cal. per mol of solute at infinite dilution

Melting point	−80.6°C
Purity	At least 70%
Specific gravity at 20°/20°C	0.79–0.80
Weight per gallon (20°C)	6.63 lbs.

Diethylamine [$(C_2H_5)_2NH$]. Diethylamine is a water-white liquid with an ammoniacal odor. It is soluble in water, ethyl alcohol, paraffin hydrocarbons, aromatic and aliphatic hydrocarbons, ethyl ether, ethyl acetate, acetone, fixed oils, mineral oil, oleic and stearic acids. It dissolves hot paraffin and carnauba waxes, which solidify when cooled. It is used as a selective solvent for the removal of impurities from oils, fats, and waxes where its property of hydrating in aqueous solution is utilized; also used in the manufacture of rubber chemicals, textile emulsions, dyes, flotation agents, resins, polymerization inhibitors, gum inhibitors, drugs and insecticides.

Typical Properties and Specifications

Boiling point	56.0°C
Critical density	0.246 g./cc.
Critical pressure	36.2 atm
Critical temperature	223.5°C
Dissociation constant	1.26×10^{-3}
Flash point (open cup)	Below 0°F
Heat of combustion	
Gas	9995 cal./g.
Liquid	9882 cal./g.
Heat of Vaporization at 58°C	91.03 cal./g.
Heat of solution in water at room temperature	8220 cal./mol of solute at infinite dilution
Melting point	−50.0°C
Specific gravity at 20/20°C	0.71
20/4°C	0.711
Specific heat of liquid at 22.5°C	0.516 cal./g.
Refractive Index at 17.6°C	1.3873
Viscosity at 25°C	0.346 centipoise
Weight per gallon (20°C)	5.89 lbs.
Distillation range	
Initial boiling point	Not below 53°C
Final boiling point	Not above 59.5°
Purity	At least 98%
Water insoluble	None

Triethylamine [$(C_2H_5)_3N$]. Triethylamine is a colorless liquid, freely soluble in water at temperatures below 18°C, soluble in ethyl alcohol, methyl alcohol, ethyl ether, ethyl acetate, aliphatic and aromatic hydrocarbons, acetone, fixed oils, mineral oil, oleic and stearic acids, and in hot carnauba and paraffin waxes, the latter two solidifying when cooled. It is used in the manufacture of corrosion inhibitors, emulsifying agents, dyestuffs, and insecticides.

Typical Properties and Specifications

Boiling point	89.5°C
Critical solution temperature (in water)	18°C
Dissociation constant	6.4×10^{-4}
Flash point (open cup)	20°F
Heat of combustion	10,248 cal./g.
Heat of solution in water	10,040 cal./mol of solute at infinite dilution
Melting point	−114.8°C
Specific gravity at 20/20°C	0.730
Refractive index at 20°C	1.4003
Weight per gallon (20°C)	6.1 lbs.
Color	Water-white
Distillation range	
Initial boiling point	Not below 85°C
Final boiling point	Not above 91°C
Purity	98.5%, min.
Water insoluble (20–30°C)	None

n-**Propylamine** (1-Aminopropane) ($CH_3CH_2CH_2NH_2$). *n*-Propylamine is a colorless liquid soluble in water, methyl and ethyl alcohols, ethyl ether, ethyl acetate, acetone, aromatic, aliphatic and paraffin hydrocarbons, fixed oils, mineral oil, oleic and stearic acids, and hot carnauba and paraffin waxes, the latter two solidifying when cooled.

Boiling point (760 mm)	49–50°C
Distillation range	46–51°C
Flash point	Below 20°F
Melting point	−83°C
Purity	95–99% (min.)
Refractive index at 20°C	1.3910
Specific Gravity at 20°C	0.718
Weight per gallon (at 20°C)	5.99 lbs.

Di-*n*-Propylamine [$(C_2H_5CH_2)_2NH$]. Di-*n*-propylamine is a colorless liquid, soluble in ethyl alcohol, methyl alcohol, ethyl ether, ethyl acetate, acetone, paraffin hydrocarbons, aliphatic and aromatic hydrocarbons, fixed oils, mineral oil, oleic and stearic acids. It dissolves hot paraffin and carnauba waxes which solidify when cooled. It is partly soluble in water.

Boiling point	110–1°C
Flash point	45°F
Melting point	−39.6°C
Purity	97% min.
Specific gravity at 20°C	0.74
Refractive index at 20°C	1.4063
Weight per gallon at 20°C	6.18 lbs.

A study[2] has been made of the solubility of di-*n*-propylamine in water and in a mixture of water and ethyl alcohol. The results of some of this work are given in Tables 10.4 and 10.5, and in Figures 10.9 and 10.10.

TABLE 10.4. MUTUAL SOLUBILITY OF DI-*n*-PROPYLAMINE AND WATER AT VARIOUS TEMPERATURES[2]

WEIGHT % AMINE	TEMP., °C.	WEIGHT % AMINE	TEMP., °C.
1.96	52.6	47.54	−1.5
2.42	44.1	60.40	4.2
2.91	36.1	64.06	8.0
5.86	12.2	73.33	17.5
9.33	−0.6	78.69	24.7
12.27	−2.2	82.15	31.2
15.28	−3.5	85.83	39.0
25.21	−4.5[a]	89.26	49.0
33.69	−4.8	93.25	74.8
44.68	−2.9		

[a] Upon cooling to −5.0° the first blue opalescence was noted at −4.9°.

TABLE 10.5. MUTUAL SOLUBILITIES OF AMINE AND ETHANOL IN WATER[2]

WEIGHT, % AMINE	WEIGHT, % ETHANOL	WEIGHT, % AMINE	WEIGHT, % ETHANOL
77.6	1.8	34.4	26.1
68.9	8.8	31.7	26.3
67.2	10.0	29.9	26.2
63.8	12.1	26.7	26.1
62.9	13.0	24.4	25.8
60.9	14.0	22.2	25.6
58.6	16.1	20.6	25.1
56.3	17.9	19.1	24.7
54.5	19.0	16.8	24.1
54.2	18.7	14.9	23.7
49.1	22.0	12.3	22.8
45.6	23.6	9.4	21.6
41.6	25.4	8.1	20.8
38.8	25.9	7.1	19.9
37.9	26.4	5.1	18.6
36.5	26.0	4.4	17.5

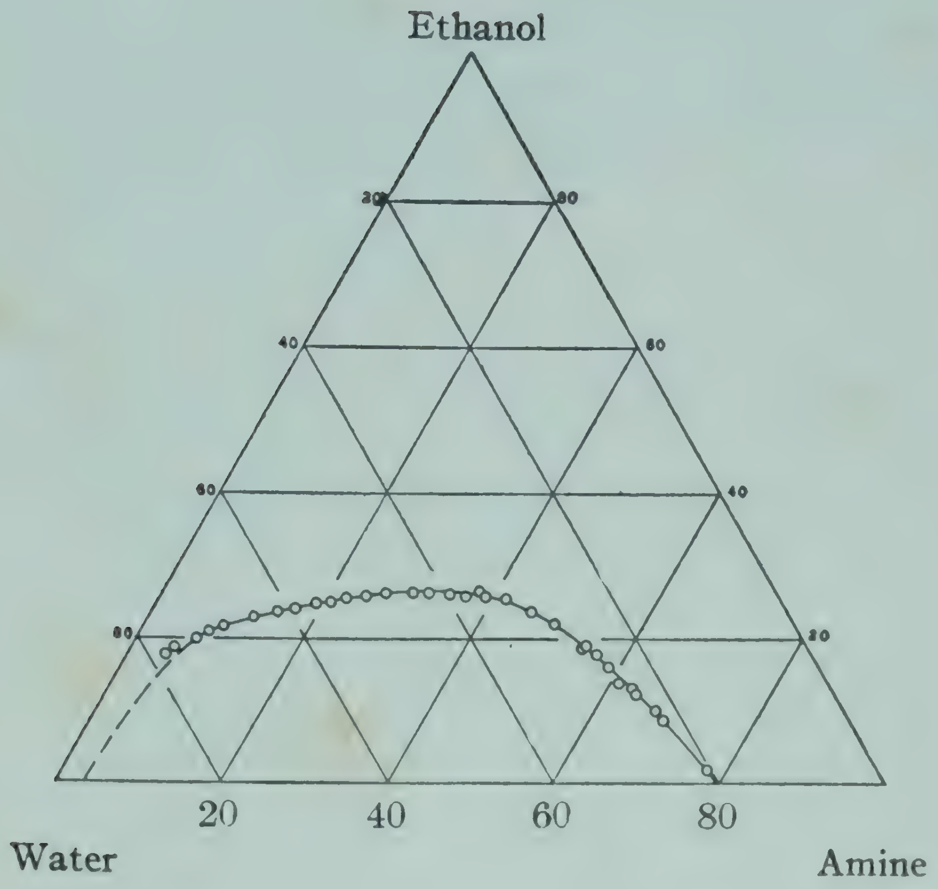


Figure 10-9. Solubility Curve at 25° for the system di-*n*-propylamine-water-ethanol.[2]

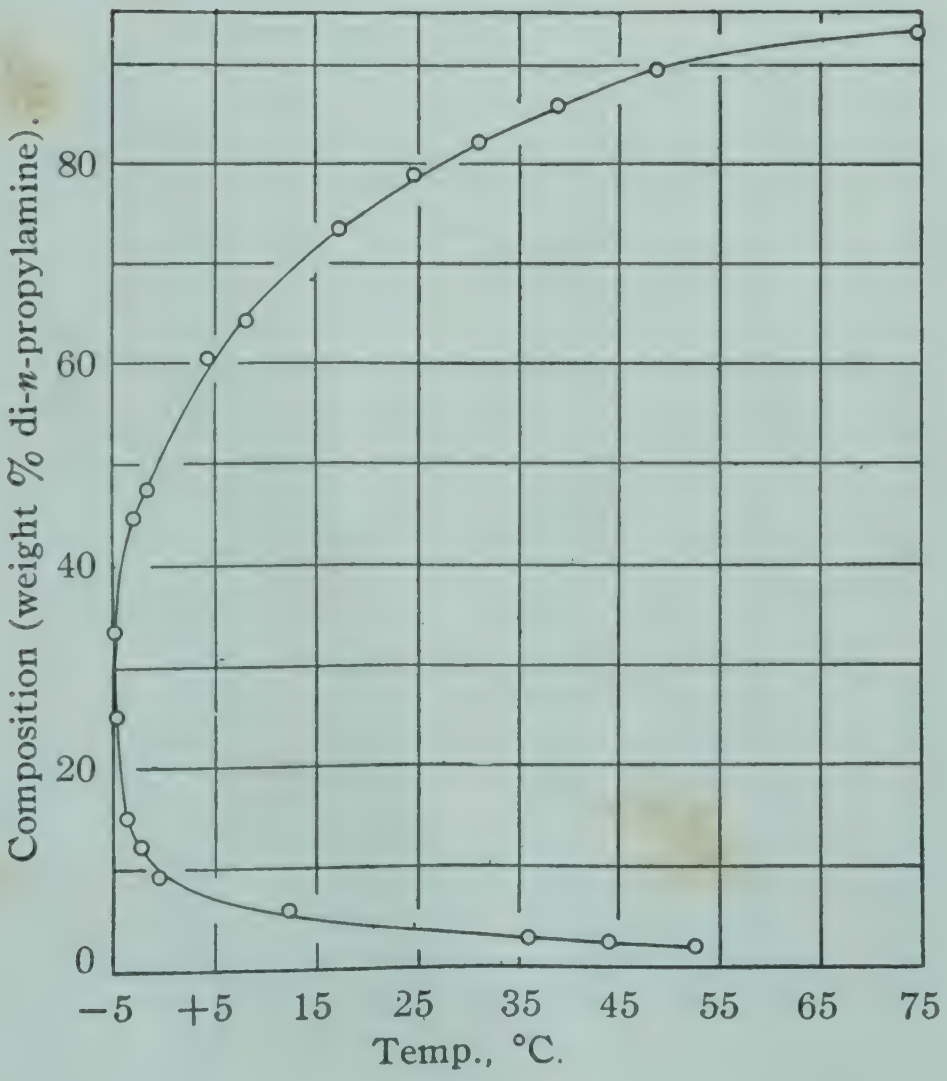


Figure 10-10. Mutual Solubility curve for the system di-*n*-propylamine-water.[2]

Isopropylamine (2-Aminopropane) ($CH_3CH(NH_2)CH_3$). This water-white, primary aliphatic amine is available commercially in an anhydrous form. It is soluble in water, methyl and ethyl alcohols, ethyl ether, ethyl acetate, aromatic and aliphatic hydrocarbons, acetone, mineral oil, fixed oils, oleic and stearic acids. It is soluble in hot paraffin and carnauba waxes, which solidify on cooling. It is potentially useful as an intermediate in such manufactured products as dyestuffs, surface-active agents, textile specialties, pharmaceuticals, bactericides, insecticides, and cleaning compounds. It is also used as an unhairing agent in the leather industry.

Boiling point	31.9°C
Flash point	<20°F
Melting point	−101.2°C
Specific gravity at 25/4°C	0.686
Vapor pressure at 15°C	385 mm
pH of 0.1 N aqueous solution	11.57
Boiling range	31–35°C
Color	Water-white

Di-Isopropylamine [$(CH_3)_2CH_2NH$]. Diisopropylamine is a water-white liquid with an amine odor. It is soluble in methyl alcohol, ethyl ether, ethyl acetate, acetone, aromatic and aliphatic hydrocarbons, mineral oil, fixed oils, oleic and stearic acids and only partly soluble in water. It dissolves hot paraffin and carnauba waxes which solidify on cooling.

Boiling range	81–85°C
Flash point	20°F
Specific gravity at 20/20°C	0.726

n-**Butylamine** (1-Aminobutane) ($CH_3CH_2CH_2CH_2NH_2$). *n*-Butylamine is a colorless liquid with an ammoniacal odor. It is miscible with water, ethyl alcohol, ethyl ether, paraffin hydrocarbons, and many organic solvents, and dissolves a wide range of materials. The butylamine salts and soaps are usually soluble in hydrocarbons. It behaves in many ways like monoamylamine, but will not produce a constant-boiling mixture with water. This compound is used in the manufacture of specialty soaps, emulsifying agents, desizing agents for textiles, rubber chemicals, flotation agents, corrosion inhibitors, dyestuffs, insecticides, and pharmaceuticals.

Typical Properties and Specifications

Boiling point (760 mm)	77.8°C
Flash point	45°C
Heat of combustion	710 kg. cal. per mol
Melting point	−50.5°C
Specific gravity at 20/20°C	0.7385
Solubility in water	Complete
Solubility of water in solvent	Complete

Refractive index at 20°C	1.4044
Viscosity at 25°C	0.68 centipoise
Vapor pressure at 20°C	0.01 mm
Weight per gallon at 20°C	6.15 lbs.
Acid insoluble	1.0% max.
Distillation range	
Initial boiling point	Not below 73.0°C
Not less than 95%	Below 82.0°C
Final boiling point	Not above 86.0°C
Purity	94% min.

***n*-Dibutylamine** [$(C_4H_9)_2NH$]. *n*-Dibutylamine is a water-white liquid with an ammoniacal odor. It is miscible with a large number and variety of organic solvents but its solubility in water is limited. It is soluble in ethyl and methyl alcohols, ethyl ether, ethyl acetate, acetone, aliphatic, and aromatic hydrocarbons, fixed oils, mineral oil, oleic and stearic acids. While it dissolves hot paraffin and carnauba waxes, these solidify on cooling. It is used in organic synthesis where its derivatives are used as flotation reagents, dyestuffs, rubber vulcanization accelerators, and corrosion inhibitors.

Typical Properties and Specifications

Boiling point	161°C
Flash point (open cup)	135°F
Specific gravity at 20/20°C	0.76
20/4°C	0.767
Refractive index at 20°C	1.4186
Vapor pressure at 20°C	2.5 mm
Weight per gallon at 20°C	6.33 lbs.
Acid insoluble	0.6% max.
Distillation range	
Initial boiling point	Not below 153°C
Not less than 95%	Below 163°C
Final boiling point	Not above 172°C
Purity	98% min.

***n*-Tributylamine** [$(C_4H_9)_3N$]. *n*-Tributylamine is a water-white to light yellow liquid with an ammoniacal odor. It is soluble in ethyl alcohol, methyl alcohol, aliphatic and aromatic hydrocarbons, ethyl acetate, acetone, fixed oils, mineral oil, oleic and stearic acids, hot carnauba and paraffin waxes, the latter two solidifying when cooled, and most organic solvents. It is almost insoluble in water. Its sulfuric acid salts are water-soluble. It is used in the manufacture of corrosion inhibitors, emulsifying agents, dyestuffs, and insecticides.

Typical Properties and Specifications

Boiling point	214°C
Coefficient of expansion per °C	0.00105
Flash point (open cup)	187°F
Melting point	−70°C
Specific gravity at 20/20°C	0.78
20/4°C	0.778
60/15°C	0.755
Refractive index at 20°C	1.431
Surface tension at 20°C	24.9 dynes/cm.
Viscosity at 25°C	1.35 centipoise
at 60°C	0.73 centipoise
Weight per gallon at 20°C	6.5 lbs.
Acid insoluble	0.25% max.
Distillation range	
Initial boiling point	Not below 203°C
Not less than 95%	Below 216°C
Final boiling point	Not above 219°C
Purity	99% min.

Isobutylamine [$(CH_3)_2CHCH_2NH_2$]. Isobutylamine is a colorless liquid soluble in water, methyl and ethyl alcohols, ethyl ether, ethyl acetate, acetone, aromatic and aliphatic hydrocarbons, fixed oils, mineral oil, oleic and stearic acids, and hot paraffin and carnauba waxes, the latter two solidifying when cooled.

Boiling point	68–9°C
Flash point	Below 20°F
Melting point	−85°C
Specific gravity at 20°C	0.731
Refractive index at 20°C	1.3985
Weight per gallon at 20°C	6.10 lbs.
Distillation range	66–69°C
Purity	99% min.

Diisobutylamine [$(C_4H_9)_2NH$]. Diisobutylamine is a colorless liquid soluble in ethyl alcohol, methyl alcohol, aromatic and aliphatic hydrocarbons, ethyl ether, ethyl acetate, acetone, fixed oils, mineral oil, oleic and stearic acids. It is insoluble in water and while it dissolves hot paraffin and carnauba waxes, these solidify on cooling.

Flash point	85°F
Melting point	−70°C
Specific gravity at 20°C	0.75
Refractive index at 20°C	1.4124
Weight per gallon at 20°C	6.22 lbs.
Distillation range	136–140°C
Purity	97% min.

sec-**Butylamine** ($CH_3CHNH_2C_2H_5$). *sec*-Butylamine is a water-white liquid with a characteristic amine odor. It is soluble in water, methyl and ethyl alcohols, ethyl ether, ethyl acetate, acetone, aromatic and aliphatic hydrocarbons, mineral oil, fixed oils, stearic and oleic acids. It dissolves hot paraffin and carnauba waxes but these solidify on cooling.

Boiling point (772 mm)	66°C
Flash point	20°F
Melting point	−104°C
Specific gravity at 20/20°C	0.725
Boiling range	62–69°C

n-**Amylamine** [$CH_3(CH_2)_4NH_2$]. *n*-Amylamine is a colorless liquid with an ammoniacal odor. Commercially it is a mixture of the following isomers, although a pure product is available.

	B.P.°C.
tert-Amylamine	82
sec-Isoamylamine	87
2-Aminopentane	89
3-Aminopentane	90
Active amylamine	94
sec-Amylamine	95
n-Amylamine	104

It is miscible with water, ethyl and methyl alcohols, ethyl ether, ethyl acetate, acetone, aromatic, and aliphatic hydrocarbons, fixed oils, mineral oil, pyridine, oleic and hot stearic acids, hot paraffin and hot carnauba waxes, the latter two solidifying when cooled. It dissolves a varied range of materials which are usually dissolved with difficulty by other organic solvents. It is used as a corrosion inhibitor and as a base for emulsifiers which are soluble in vegetable and mineral oils. It is also employed in textile lubrication, and as a raw material in the manufacture of dyestuffs, emulsifying agents, antioxidants, desizing agents for textiles and pharmaceuticals.

Typical Properties and Specifications

Boiling point	102–104°C
Coefficient of expansion at 20–60°C	0.00116
Constant-boiling mixture	
n-Amylamine	79–82.5% 82–85°C B.P.
Water	21–17.5%
Flash point (open cup)	65°F
Heat of vaporization	108 cal./g.
Melting point	−55°C
Specific gravity at 20/20°C	0.76–0.78
Specific heat at 60°F	0.65 cal./g.
Refractive index at 19°C	1.4068
Surface tension at 13°C	24.4 dynes/cm.

Viscosity at 20°C	0.01018 poise
Vapor pressure at 26°C	35 mm
Weight per gallon at 20°C	6.41 lbs.
Color	Water-white
Distillation range	
Initial boiling point	Not below 84°C
Not less than 95%	Below 100°C
Final boiling point	Not above 110°C
Purity	90% min.
Water dilution	20:1 min.

Diamylamine (Mixed Isomers) [$(C_5H_{11})_2NH$]. Diamylamine is a colorless to straw-colored liquid with an ammoniacal odor, which is composed of a mixture of amyl isomers. It is soluble in ethyl alcohol, methyl alcohol, ethyl ethers, ethyl acetate, acetone, aromatic and aliphatic hydrocarbons, fixed oils, mineral oil, oleic and stearic acids. It is insoluble in water and while soluble in hot paraffin and carnauba waxes, these solidify on cooling. It is a solvent for oils, resins, and some cellulose esters. Introduction of the amyl group imparts oil solubility to otherwise oil-insoluble substances. It is used as a corrosion inhibitor, and in chemical synthesis.

Typical Properties and Specifications

Coefficient of expansion at 20–60°C	0.00102
Flash point (open cup)	158°F
Heat of vaporization	83 cal./g.
Specific gravity at 20/20°C	0.77–0.78
Specific heat at 60°F	0.54 cal./g.
Refractive index at 20°C	1.4259
Surface tension at 13°C	24.4 dynes/cm.
Vapor pressure at 26°C	9 mm
Viscosity at 20°C	0.01264 poise
Weight per gallon at 20°C	6.45 lbs.
Acid insoluble	0.5% min.
Distillation range	
Initial boiling point	Not below 175°C
Not less than 95%	Below 202°C
Final boiling point	Not above 218°C
Purity	99% min.
Sulfur	0.06% min.

Triamylamine (Mixed Isomers) [$(C_5H_{11})_3N$]. Triamylamine is a water-white to light-yellow, stable liquid which is strongly basic in reaction. It is soluble in ethyl alcohol, ethyl ether, ethyl acetate, acetone, aromatic and aliphatic hydrocarbons, fixed oils, mineral oil, oleic and stearic acids, and in hot paraffin and carnauba waxes, the latter two solidifying when cooled. It is insoluble in water and methyl alcohol. It is an excellent corrosion inhibitor of steel in a 0.13 per cent solution in normal sulfuric acid. It is used in the manufacture of emulsifying agents, dyestuffs, and insecticides.

Coefficient of expansion	0.00091
Flash point (open cup)	215°F
Heat of vaporization	79 cal./g.
Specific gravity at 20/20°C	0.79–0.80
Specific heat at 60°F	0.51 cal./g.
Refractive index at 18°C	1.4374
Surface tension at 13°C	24.4 dynes/cm.
Viscosity at 20°C	0.02421 poise
Vapor pressure at 26°C	7 mm
Weight per gallon at 20°C	6.60 lbs.
Acid insolubles	1.0% max.
Distillation range	
Initial boiling point	Not below 234°C
Not less than 50%	Above 244°C
Not less than 95%	Below 256°C
Final boiling point	Not above 260°C
Purity	99% min.

sec-**Amylamine** [$CH_3CH(NH_2)C_3H_7$]. *sec*-Amylamine is a colorless liquid with an amine odor. It is soluble in water, methyl and ethyl alcohols, aromatic and aliphatic hydrocarbons, ethyl ether, ethyl acetate, acetone, fixed oils, oleic and stearic acids. It dissolves hot paraffin and carnauba waxes which solidify when cooled.

Boiling point (760 mm)	91–92°C
Flash point	20°F
Specific gravity at 20°C	0.739
Refractive index at 20°C	1.4047
Weight per gallon at 20°C	6.15 lbs.
Distillation range	89–92°C
Purity	95–99% min.

sec-**Hexylamine** ($CH_3CHNH_2C_4H_9$). *sec*-Hexylamine is a colorless liquid with an amine odor and soluble in water, ethyl alcohol, and paraffin hydrocarbons.

Flash point	55°F
Specific gravity at 20°C	0.746
Weight per gallon	6.22 lbs.
Distillation range	107–110°C
Purity	95–99%

2-Ethylbutylamine (Hexylamine) [$(C_2H_5)_2CHCH_2NH_2$]. 2-Ethylbutylamine is a water-white liquid with an amine odor. It is soluble in methyl and ethyl alcohols, ethyl ether, ethyl acetate, acetone, aromatic and aliphatic hydrocarbons, fixed oils, mineral oil, oleic and stearic acids. It dissolves in water and while soluble in hot paraffin and carnauba waxes, these solidify on cooling.

Flash point	70°F
Specific gravity at 20/20°C	0.776
Boiling range	121–125°C

n-**Heptylamine** ($C_7H_{15}NH_2$). *n*-Heptylamine is a water-white liquid with an amine odor. It is insoluble in water but soluble in ethyl and methyl alcohols, ethyl ether, ethyl acetate, acetone, aromatic and aliphatic hydrocarbons, fixed oils, mineral oil, oleic and stearic acids. It dissolves hot paraffin and carnauba waxes, which solidify when cooled.

Flash point	130°C
Melting point	−23°C
Specific gravity at 20/20°C	0.779
Boiling range	150–160°C

2-Ethylhexylamine (Octylamine) ($C_4H_9C_2H_5CHCH_2NH_2$). Octylamine is a water-white liquid with an amine odor. It is insoluble in water but soluble in methyl alcohol, ethyl ether, ethyl acetate, acetone, aromatic and aliphatic hydrocarbons, fixed oils, mineral oil, oleic and stearic acids. It dissolves hot paraffin and carnauba waxes, which solidify on cooling.

Flash point	135°F
Specific gravity at 20/20°C	0.792
Boiling range	165–169°C

Di-2-Ethylhexylamine (Dioctylamine) $[(C_4H_9CH(C_2H_5)CH_2)_2NH]$. Dioctylamine is a colorless liquid with a faintly amine odor. It is soluble in methyl alcohol, ethyl ether, ethyl acetate, acetone, aromatic and aliphatic hydrocarbons, fixed oils, mineral oil, oleic and stearic acids. It is insoluble in water and while soluble in hot paraffin and carnauba waxes, these solidify when cooled. Among the large number of substances it will dissolve are natural and synthetic resins.

Boiling point (760 mm)	281.1°C
Flash point	270°C
Specific gravity at 20/20°C	0.8062
Solubility in water at 20°C	0.02% by wt.
Solubility of water in solvent at 20°C	0.17% by wt.
Vapor pressure at 20°C	0.01 mm
Weight per gallon at 20°C	6.71 lbs.
Boiling range	269–280°C

Mono-*n*-Butyl Diamylamine $[C_4H_9N(C_5H_{11})_2]$. This amine is a light-straw colored liquid with an amine odor. It is soluble in acetone, ethyl ether, ethyl acetate, aromatic and aliphatic hydrocarbons, fixed oils, mineral oil, and oleic and stearic acids. It is insoluble in water, methyl alcohol, and although soluble in hot paraffin and carnauba waxes, these solidify on cooling.

Flash point	200°F
Specific gravity at 20/20°C	0.788
Weight per gallon at 20°C	6.56 lbs.
Boiling range	229–241°C

ALKYLENE DIAMINES

Ethylenediamine ($NH_2CH_2CH_2NH_2$). Ethylenediamine is a water-white, hygroscopic liquid with a strong ammoniacal odor. The commercial product is a 78% solution of ethylenediamine by weight. It is used in the synthesis of organic rubber accelerators, insecticides, textile processing chemicals, emulsifiers, plastics and pharmaceuticals. It is also used as a corrosion inhibitor.

Typical Properties and Specifications
78% solution

Boiling point (760 mm)	117.2°C
Dielectric constant at 18°C	16.0
Flash point (open cup)	110°F
Heat of combustion	425.6 cal./mol
Heat of solution at 15°C	7.6 cal./mol
Ionization constant at 25°C	7.1×10^{-5}
Latent heat of evaporization	167 cal./g.
Latent heat of fusion (0°C)	77 cal./g.
Melting point	11.0°C
Specific gravity at 20/20°C	0.8995
Solubility in water at 20°C	Complete
Solubility of water in solvent at 20°C	Complete
Refractive index at 26°C	1.4540
Vapor pressure at 20°C	10.7 mm
Viscosity at 25°C	0.0154 poise
Weight per gallon at 20°C	7.49
Constant-boiling mixture	
Ethylenediamine	80% by wt. B.P.°C
Water	20% by wt. 118.5
Boiling range (760 mm)	115 to 122°C
Color	Water-white
Purity	78% by wt.

Propylenediamine (1,2-Diaminopropane) [$(CH_3CH(NH_2)CH_2NH_2$]. Propylenediamine is a water-white liquid with an ammoniacal odor. It is miscible with water and many organic solvents, among them being benzene and naphtha. It does not form a constant-boiling mixture with water. It is a solvent for such substances as cellulose nitrate, castor oil, shellac, pine oil, copal gum, rosin, and dyes. It behaves much like ethylenediamine but it is considered superior in solvent power. It is used in the manufacture of gasoline additives.

Boiling point (760 mm)	119.7°C
Flash point (open cup)	120°F
Specific gravity at 20/20°C	0.8732
Solubility in water at 20°C	Complete
Solubility of water in solvent at 20°C	Complete
Vapor pressure at 20°C	9.4 mm
Weight per gallon at 20°C	7.27 lbs.
Boiling range (760 mm)	112–122°C
Purity	80% by wt. min.

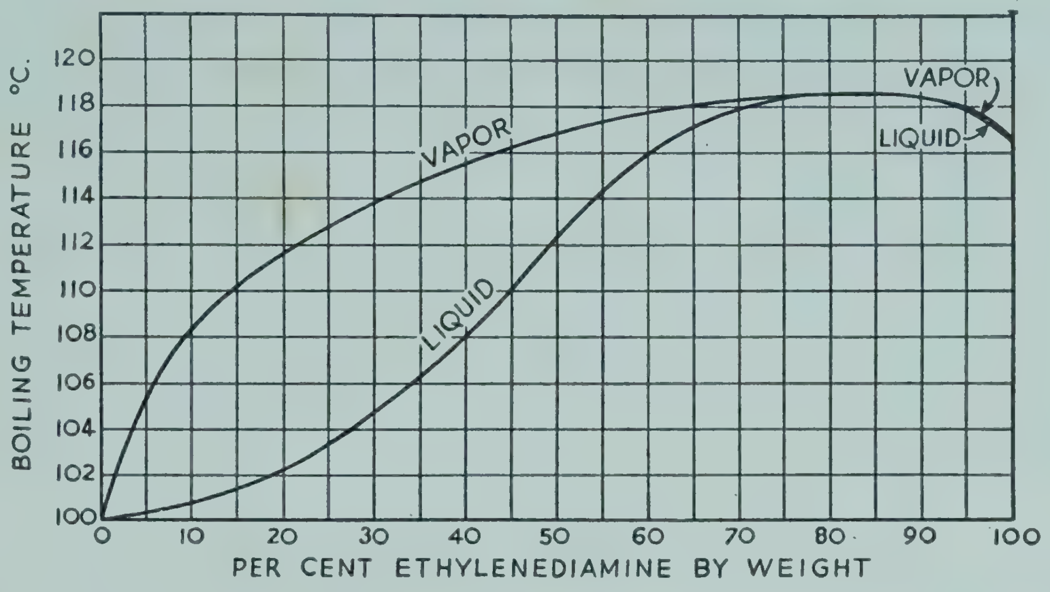


Figure 10-11. Boiling-Point Composition Curves for Aqueous Ethylenediamine Solutions.

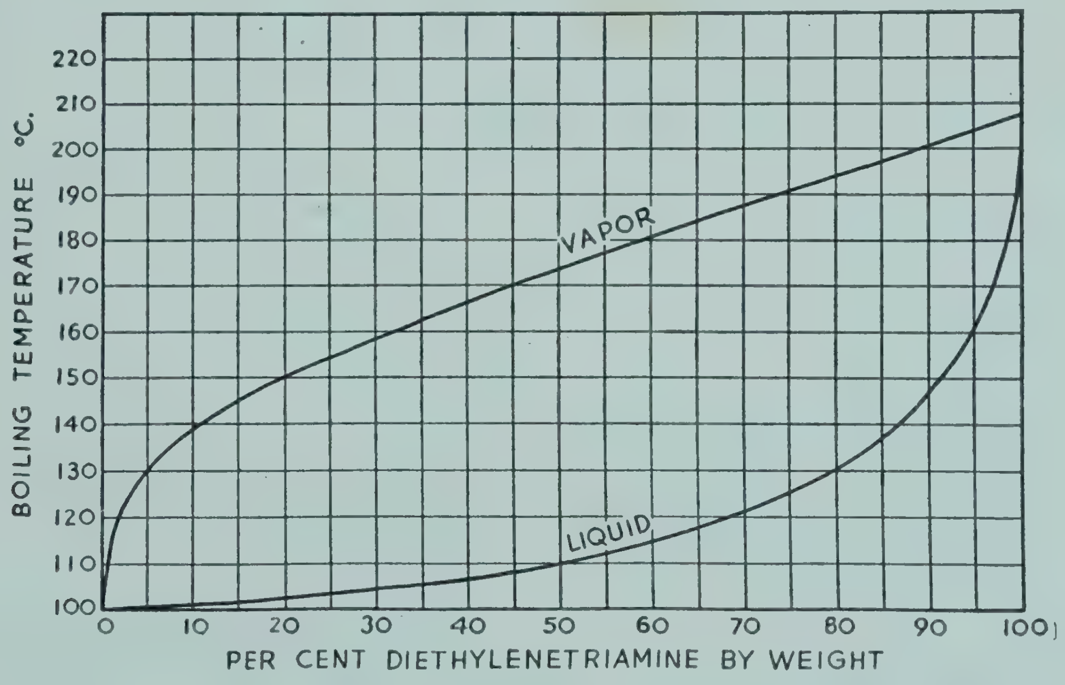


Figure 10-12. Boiling-Point Composition Curves for Aqueous Diethylenetriamine Solutions.

Diethylenetriamine ($NH_2CH_2CH_2NHCH_2CH_2NH_2$). Diethylenetriamine is a colorless liquid, completely miscible with water and many organic solvents. It is a solvent for sulfur, acid gases, numerous natural resins and dyes. It is also used in organic synthesis and as a saponification agent for acidic materials.

Boiling point (760 mm)	207.1°C
Flash point (open cup)	215°F
Specific gravity at 20/20°C	0.9542
Vapor pressure at 20°C	0.03 mm
Weight per gallon at 20°C	7.94 lbs.

Tetraethylenepentamine [$NH_2(CH_2CH_2NH)_3CH_2CH_2NH_2$]. Tetraethylenepentamine is a viscous, hygroscopic and high-boiling liquid. It is miscible with water and many organic solvents, and is a solvent for dyes, resins, sulfur and acid gases. It also forms soaps with fatty acids and it is employed in the synthesis of emulsifiers, plastics and in rubber reclaiming.

Boiling point (760 mm)	333°C
Flash point	325°F
Specific gravity at 20°C	0.998
Vapor pressure at 20°C	0.01 mm
Weight per gallon at 20°C	8.31 lbs.
Boiling range (760 mm)	320°–360°C

ARYLAMINES

Aniline (Aminobenzene, phenylamine) ($C_6H_5NH_2$). Aniline is a colorless to straw-colored, toxic, highly refractive, oily liquid having a characteristic odor. It is soluble in ethyl alcohol, ethyl ether, carbon tetrachloride, and only slightly soluble in water. It is used in the production of such materials as indigo, aniline black, tetranitraniline, acetanilide, explosives, dyes, rubber chemicals, and pharmaceuticals.

Boiling point	184.2°C
Flash point	70°C
Freezing point	−6.3°C min.
Melting point	−6.2°C
Specific gravity at 25/25°C	1.021
Solubility in water at 25°C	3.8
80°C	6.0
Weight per gallon at 25°C	8.50 lbs.
Boiling range	1.5°C 95% distills within 1.0°C
Nitrobenzene	None

Dimethylaniline [$C_6H_5N(CH_3)_2$]. Dimethylaniline is a pale, yellow highly refractive, toxic, oily liquid with a pungent odor. It is soluble in ethyl alcohol, ethyl ether, and carbon tetrachloride, but only very slightly soluble in water. It is used in the making of dyes and the explosive tetranitroaniline ("Tetryl").

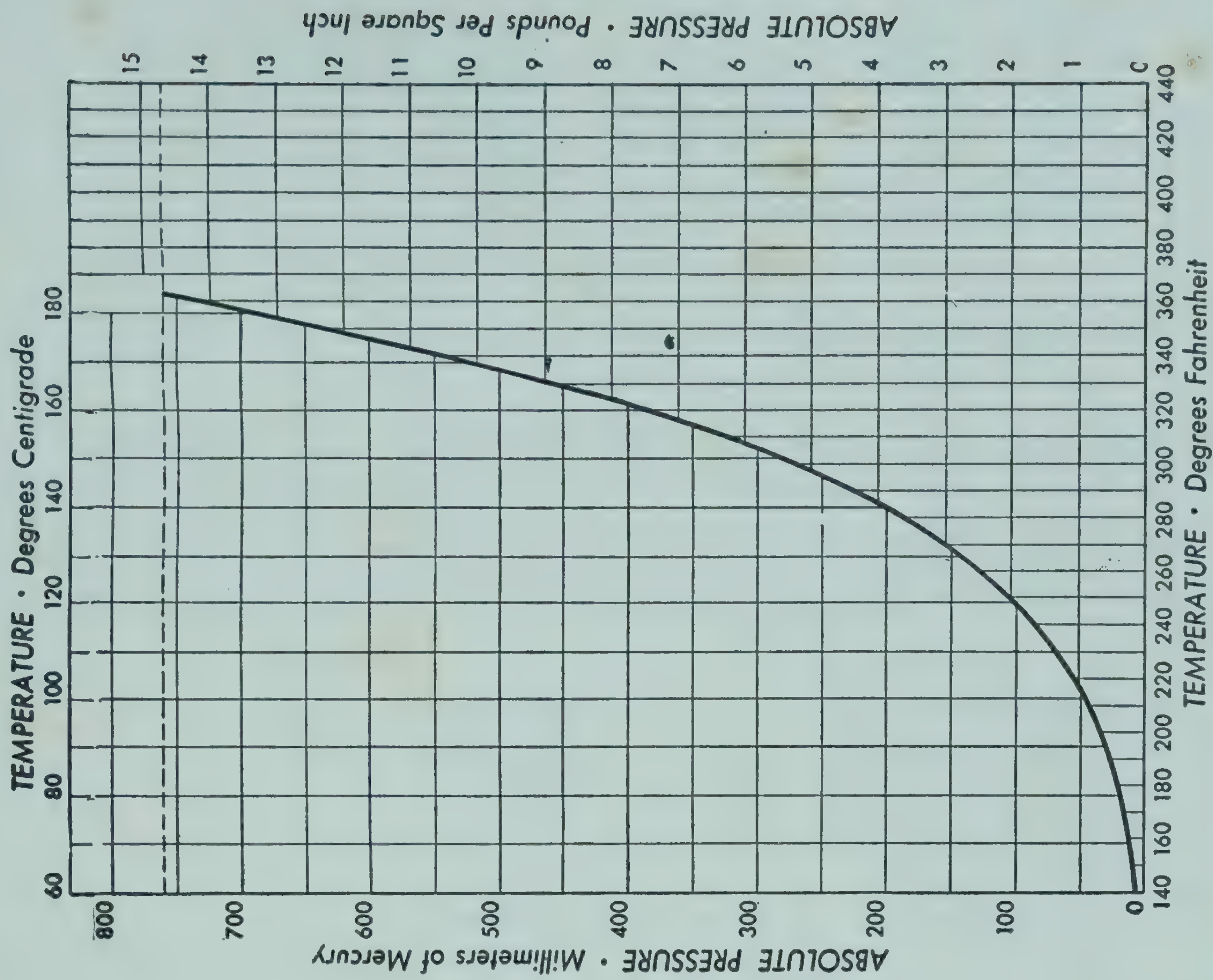


Figure 10-14. Vapor Pressures of Dimethylaniline.

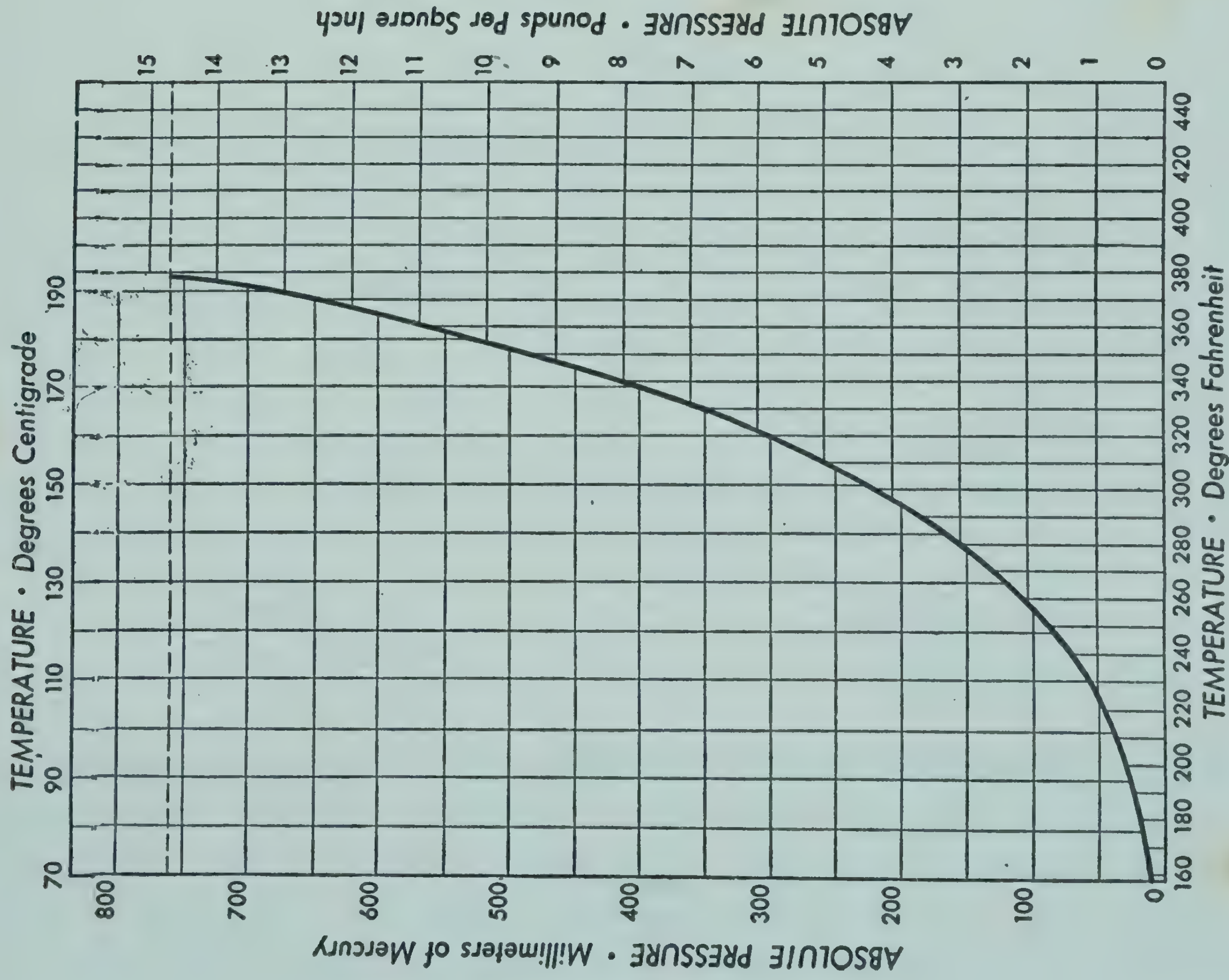


Figure 10-13. Vapor Pressures of Aniline Oil.

Boiling point	192.9°C
Freezing point	1.5°C
Specific gravity at 25/25°C	0.956
Weight per gallon at 25°C	7.95 lbs.
Boiling range within	2.0°C 95% distills within 1.0°C
Color	Yellow to amber
Monomethylaniline	0.5% max.

Diethylaniline [$C_6H_5N(C_2H_5)_2$]. Diethylaniline is a light-yellow, oily, toxic liquid with a pungent odor. It is soluble in ethyl alcohol, ethyl ether, and carbon tetrachloride but only very slightly soluble in water. It is used in the preparation of dyes, pharmaceuticals, and other organic compounds.

Boiling range	216.3°C
Freezing point	−34.4°C
Specific gravity at 25/25°C	0.933
Weight per gallon at 25°C	7.76 lbs.
Aniline	None
Boiling range	5–95% within 2.5°C Boiling range includes 216.3°C
Color	Light yellow
Monoethylaniline	0.2% max.
Purity	99.8%, min.
Water	No visible separation

N-Mono-*n*-Butyl Aniline ($C_6H_5NHC_4H_9$). This secondary amine is a light straw to amber-colored liquid with an aniline odor. It is insoluble in water but soluble in ethyl alcohol, methyl alcohol, ethyl ether, ethyl acetate, acetone, aromatic and aliphatic hydrocarbons, fixed oils, mineral oil, oleic acid, and hot stearic acid. It is also soluble in hot paraffin and carnauba waxes which solidify on cooling.

Flash point	225°F
Specific gravity at 20°C	0.93
Refractive index at 20°C	1.5351
Weight per gallon at 20°C	7.71 lbs.
Boiling range	234–242°C
Purity	95%, min.

N,N-Di-*n*-Butyl Aniline [$C_6H_5N(C_4H_9)_2$]. N,N-Di-n-Butyl aniline is a light-straw colored liquid with a faintly aniline odor and soluble in ethyl alcohol, aromatic hydrocarbons, ethyl ether, ethyl acetate, acetone, fixed oils, mineral oil, oleic acid and hot stearic acid. It is insoluble in water, methyl alcohol, and while soluble in hot paraffin and carnauba waxes, these solidify when cooled.

Flash point	230°F.
Specific gravity at 20°C	0.904
Refractive index at 20°C	1.5197
Weight per gallon at 20°C	7.53 lbs.
Boiling range	267–275°C
Purity	95%, min.

***n*-Monoamyl Aniline** (Mixed Isomers) ($C_6H_5NHC_5H_{11}$). *n*-Monoamyl aniline is a mixture of isomers. It is a light-straw colored liquid with a faintly aniline odor. It is insoluble in water but soluble in ethyl alcohol, methyl alcohol, ethyl ether, ethyl acetate, acetone, aromatic and aliphatic hydrocarbons, fixed oils, mineral oil, oleic acid, and hot stearic acid. It is also soluble in hot paraffin and carnauba waxes which solidify on cooling.

Flash point	225°F
Specific gravity at 20°C	0.92
Refractive index at 20°C	1.5285
Weight per gallon at 20°C	7.64 lbs.
Boiling range	245–260°C
Purity	95%, min.

***p-tert*-Amyl Aniline** ($C_5H_{11}C_6H_4NH_2$). *p-tert*-Amyl aniline, an aryl amine, is a straw to deep red-colored liquid with a faintly aromatic odor. It is soluble in methyl alcohol, ethyl ether, ethyl acetate, acetone, aromatic and aliphatic hydrocarbons, fixed oils, mineral oil, oleic acid and hot stearic acid. It is insoluble in water and while it dissolves hot carnauba and paraffin waxes, these solidify on cooling.

Flash point	215°F
Specific gravity at 20/20°C	0.948
Boiling range	253–259°C

Di-*tert*-Amyl Aniline [$(C_5H_{11})_2C_6H_3NH_2$]. Di-*tert*-amyl aniline, an arylamine, is a red-colored, almost odorless liquid, soluble in ethyl ether, ethyl acetate, acetone, aromatic and aliphatic hydrocarbons, fixed oils, mineral oil, oleic acid and hot stearic acid. It is insoluble in water and methyl alcohol, and dissolves hot carnauba and paraffin waxes, which solidify when cooled.

Flash point	265°F
Specific gravity at 20/20°C	0.923
Boiling range	289–321°C

N,N-Diamyl Aniline (Mixed Isomers) [$C_6H_5N(C_5H_{11})_2$]. N,N-Diamylaniline is a dark-amber liquid with a faintly aniline odor. It is insoluble in methyl alcohol, and water but soluble in ethyl ether, ethyl acetate, acetone, aromatic and alphatic hydrocarbons, fixed oils, mineral oil, oleic acid, and hot stearic acid. It is also soluble in hot carnauba and paraffin waxes, which solidify on cooling.

Flash point	260°F
Specific gravity at 20/20°C	0.898
Boiling range	276–292°C

Diethylbenzylamine [$C_6H_5CH_2N(C_2H_5)_2$]. Diethylbenzylamine is a colorless liquid with an almond-like odor. It is soluble in ethyl and methyl alcohols, ethyl ether, ethyl acetate, acetone, aromatic hydrocarbons, fixed oils, mineral oil, oleic acid and hot stearic acid. It is insoluble in water and while soluble in hot paraffin and carnauba waxes, these solidify on cooling.

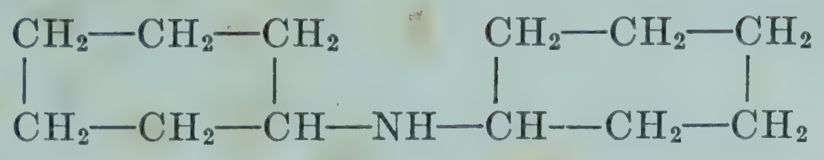
Flash point	170°F
Specific gravity at 20°C	0.890
Refractive index at 20°C	1.5002
Weight per gallon at 20°C	7.41 lbs.
Boiling range	207–215°C
Purity	97%, min.

Cyclohexylamine $\underbrace{(CH_2CH_2CH_2CH(NH_2)\text{-}CH_2CH_2)}$. Cyclohexylamine is a colorless, caustic liquid with a fishy, amine odor. It has been known since 1893, but not until 1936 was it made in commercial quantities in the United States. It is produced by the catalytic hydrogenation of aniline. It is a strong base, even stronger than ammonia or the ethanolamines. It is miscible with water and most of the common organic solvents, among which are the alcohols, ethers, ketones, esters, aliphatic and aromatic hydrocarbons, both pure and chlorinated. It is used as a solvent and as a corrosion inhibitor. Either alone or as a soap, it is employed as a wetting-out, cleansing, washing, emulsifying or dispersing agent in the textile industry. It may be used to absorb acidic gases, as a preservative for dyes, as an insecticide, and in the printing and dyeing of textile products.

Typical Properties and Specifications

Boiling point (760 mm)	134.5°C
Freezing point	−17.7°C
Fire point	30°C
Flash point	Below 0°C
Specific gravity at 25/25°C	0.8647
Refractive index at 25°C	1.4565
Weight per gallon at 20°C	7.206 lbs.
Azeotropic mixture	
Cyclohexylamine	44.2% by wt. B.P. (760 mm) 96.4°C
Water	55.8% by wt.
Distillation range	132.0–137.5°C
Purity	98.0% min.

Dicyclohexylamine



Dicyclohexylamine is a clear, colorless and strongly basic liquid with a faint odor. It is miscible with most organic solvents but only slightly soluble in water. Unlike cyclohexylamine, it does not form an azeotropic mixture with water. It is more toxic than cyclohexylamine when absorbed through the skin and when large amounts are absorbed, death may result.

Dicyclohexylamine soaps are good emulsifying agents. This solvent may be used to absorb acidic gases, to preserve rubber latex, to plasticize casein, to neutralize plant and insect poisons, and as a solvent for dyes in the textile printing and dyeing industry.

Typical Properties and Specifications

Boiling point (760 mm)	255.8°C
Freezing point	−0.1°C
Fire point	160°C
Flash point	100°C
Specific gravity at 25/25°C	0.9104
Refractive index at 25°C	1.4823
Weight per gallon at 20°C	7.59 lbs.
Boiling range	252.0–258.0°C
Purity	98%, min.

N-(*n*-Butyl)Alpha-naphthylamine ($C_{10}H_7NHC_4H_9$). This solvent is a dark-red liquid with a faintly amine odor. It is a solvent for methyl alcohol, ethyl ether, ethyl acetate, acetone, aromatic and aliphatic hydrocarbons, fixed oils, mineral oil, oleic and hot stearic acid. It is insoluble in water, and soluble in hot paraffin and carnauba waxes which solidify on cooling.

Flash point	295°F
Specific gravity at 20/20°C	1.012
Boiling range	318–325°C

Pyridine ($\underline{\mathrm{CH{=}CH{-}CH{=}N{-}CH{=}CH}}$). Pyridine is a liquid miscible with water, alcohol, ether, benzene and many organic liquids. It is an excellent solvent for organic materials and will dissolve many metallic salts giving comparatively stable compounds (without substitution). It is used in the preparation of water-proofing chemicals, rubber accelerators, and pharmaceuticals. It is also used as an extractant and in distilling and purifying operations. The less pure grade is used as a denaturant for industrial alcohol.

Boiling point	115°C
Melting point	−42°C
Specific gravity at 25/4°C	0.978

2,4-Lutidine (Dimethyl pyridine) $(\underline{N{=}C(CH_3){-}CH{=}C(CH_3){-}CH{=}CH})$. 2,4-Lutidine is a liquid, very soluble in alcohols, ketone, ethers, hydrocarbons and most organic solvents but only 15 per cent soluble in water. It is recommended for use in the synthesis of drugs, dyes and other chemicals.

Boiling point	158.3°C
Distillation	90% distills within 2°C
Freezing point	Below −60°C
Specific gravity at 25/4°C	0.927

2,6-Lutidine (Dimethyl pyridine) $[(\underline{N{=}C(CH_3){-}CH{=}CH{-}CH{=}C}(CH_3))]$. 2,6-Lutidine is a liquid, very soluble in water, alcohols, ethers, ketones, hydrocarbons and most organic solvents. It is recommended for use in the manufacture of resins, dyes, drugs, insecticides, rubbers, and organic chemicals.

Boiling point	142.9°C
Freezing point	−6.0°C
Purity	95%, min.
Specific gravity at 25/4°C	0.928

Alpha-Picoline (Methyl pyridine) $[\underline{N{=}C(CH_3){-}CH{=}CH{-}CH{=}CH}]$. Alpha-picoline is a liquid which is very soluble in water, forming a constant-boiling mixture with it. It is also soluble in ethyl alcohol and ethyl ether. It may be used in the manufacture of alkaloids, pharmaceuticals, antioxidants, and rubber accelerators.

Boiling point	128°C
Melting point	−69.9°C
Specific gravity at 15/4°C	0.950
Distillation Range	Completely within 2°C

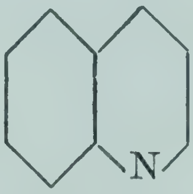
Beta-Picoline (Methyl pyridine) $[\underline{N{=}CH{-}C(CH_3){=}CH{-}CH{=}CH}]$. Beta-picoline is similar to the alpha compound. It is soluble in water with which it forms a constant-boiling mixture; it is also soluble in ethyl alcohol and ethyl ether. Suggested uses for it are in the manufacture of alkaloids, pharmaceuticals and rubber accelerators. It is also a starting material for the production of nicotinic acid and nicotinic acid amide.

Boiling point	143.5°C
Melting point	−18.3°C
Purity	95%, min.
Specific gravity at 15/4°C	0.961

Gamma-Picoline (Methyl pyridine) ($N{=}CH{=}CH{=}C(CH_3)$-—CH—CH). The solubility and uses for this solvent are similar to those of the alpha and beta compounds.

Boiling point	143.1°C
Melting point	+3.8°C
Purity	95%, min.
Specific gravity at 15/4°C	0.957

Quinoline



Quinoline is a liquid, soluble in alcohol, ether, carbon disulfide and in most of the common organic solvents, but only partially soluble in water. It is a solvent for cellulose esters and ethers when used with other solvents. It is used in the manufacture of dyes, photographic sensitizers, nicotinic acid, and drugs. It is also used as an extraction agent and in organic synthesis.

Boiling point	237.7°C
Melting point	−19.5°C
Specific gravity at 20/4°C	1.095
Distillation range	95% distills within 2°C

ALKANOLAMINES

The most important members of this group from a commercial standpoint are monoethanolamine, diethanolamine and triethanolamine. Also available in commercial quantities are the aminohydroxy derivatives of nitroparaffins, i.e., 2-amino-1-butanol, 2-amino-2-methyl-1-propanol, 2-amino-2-methyl-1,3-propanediol, 2-amino-2-ethyl-1,3-propanediol, and tris (hydroxymethyl) aminomethane.

These compounds are used as emulsifiers for cosmetic lotions and creams, mineral oil and paraffin wax emulsions, textiles, leather dressings, cleaning compounds, polishes, and "soluble oils". They are also used in the manufacture of pharmaceuticals, surface-active and wetting agents, vulcanization accelerators, photographic developers, dyestuffs, and resins. Having the property of absorbing acidic gases, such as H_2S and CO_2 in cold aqueous solutions and releasing them when hot, these compounds suggest usefulness in gas recovery and purification. They also form the basis for chemical synthesis.

Monoethanolamine [2(Hydroxyethyl)amine, 2-aminoethanol, collamine $H_2NCH_2CH_2OH$]. Monoethanolamine is a somewhat viscous hygroscopic liquid with an ammoniacal odor. It is miscible with water and many organic solvents. Its molecule contains both a hydroxyl and an amine group, thus producing derivatives that have characteristics of both types of compounds. It is used as a softener and conditioning agent, and in the recovery and extraction of carbon dioxide and hydrogen sulfide from industrial gases. Its soaps with fatty acids are excellent emulsifiers for waxes. It is also utilized as an intermediate in the manufacture of rubber accelerators and dyestuffs.

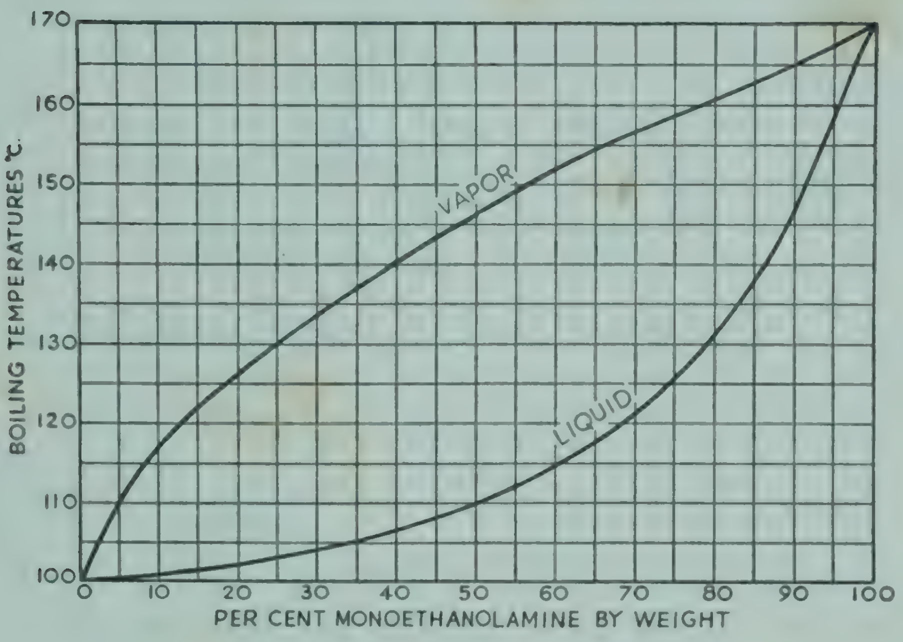


Figure 10-15. Boiling-Point Composition Curves for Aqueous Monoethanolamine Solutions.[4]

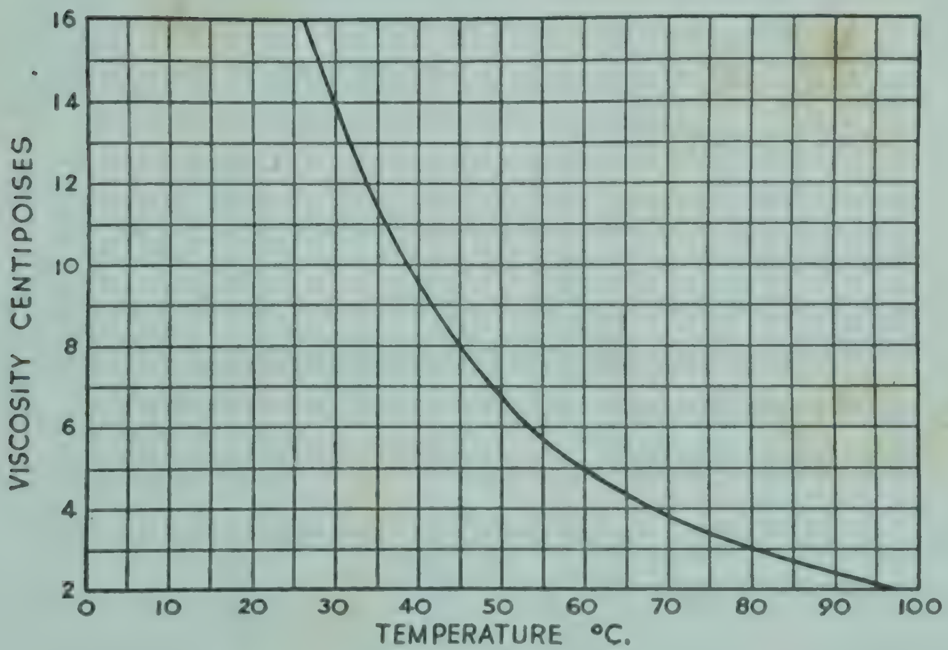


Figure 10-16. Viscosity of Monoethanolamine at Various Temperatures.[4]

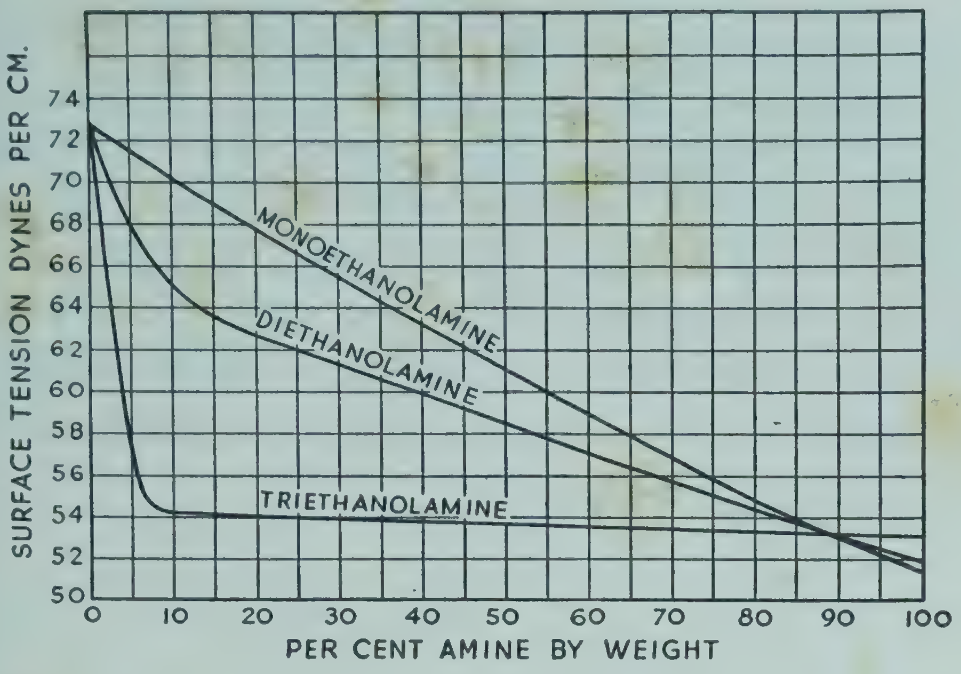


Figure 10-17. Surface Tension of Aqueous Ethanolamine Solutions at 20°C.[4]

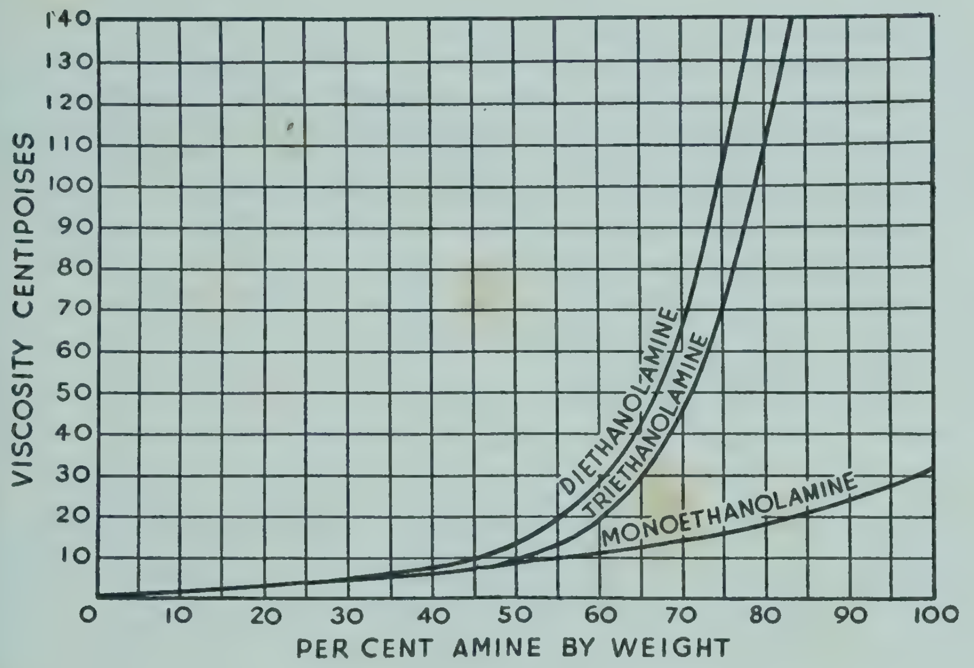


Figure 10-18. Viscosity of Aqueous Ethanolamine Solutions at 20°C.[4]

Typical Properties and Specifications

Boiling point	172.2°C
Coefficient of expansion at 20°C	0.000770 (per°C)
Dissociation constant at 20°C	5×10^{-5}
Equivalent weight	61 to 63
Flash point (open cup)	93°C (200°F)
Heat of evaporization at B.P	199 cal/g
Refractive index at 20°C	1.4539
Specific gravity at 20/20°C	1.0180
Specific heat at 30°C	0.665 cal/g
Surface tension at 20°C	51 dynes/cm
Viscosity at 20°C	3.40 poises
Vapor pressure at 20°C	0.67 mm Hg
Weight per gallon at 20°C	8.472 lbs
Boiling range at 760 mm	Not less than 90% over between 165 and 173°C
Color	Water-white
pH 25% Solution at 25°C	12.1
Solubility in water	Complete

Diethanolamine [Di-2-hydroxyethylamine, $(HOCH_2CH_2)_2NH$].[4] "When pure, diethanolamine is a crystalline, white solid which has a melting point of 28°C, or just above room temperature. The commercial material has a mild, ammoniacal odor. Like other ethanolamines, Diethanolamine enters into reactions characteristic of both amines and alcohols; its most important property is its ability to combine directly with acids and acidic gases. At normal temperatures, its aqueous solutions have a strong affinity for hydrogen sulfide and carbon dioxide; and at higher temperatures, this affinity decreases, with expulsion of the gases.

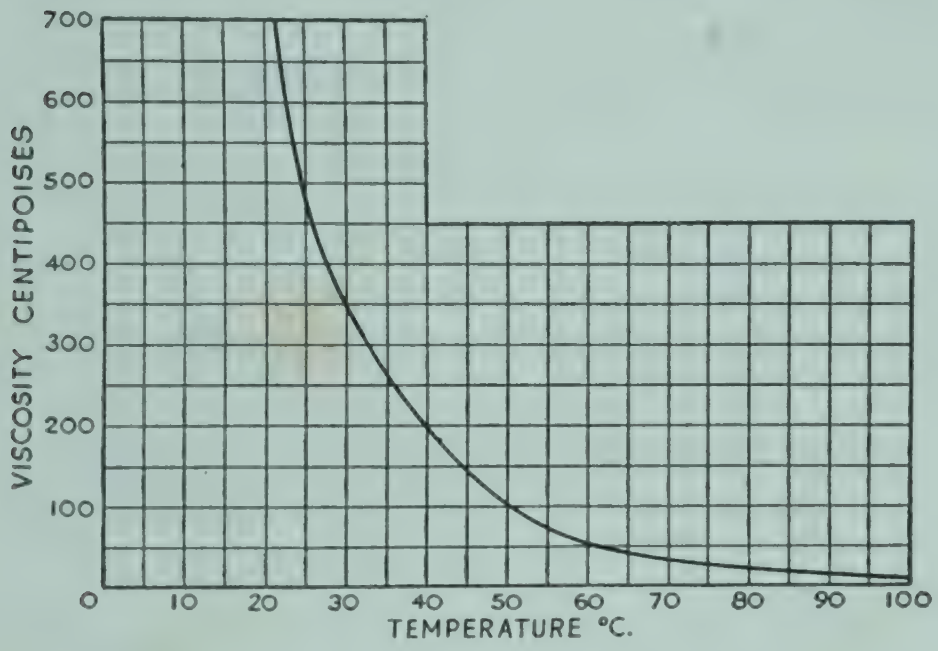


Figure 10-19. Viscosity of Diethanolamine at Various Temperatures.

"Diethanolamine finds wide use as an absorbent for acidic gases; especially for the removal, recovery, and concentration of carbon dioxide from flue and other waste gases as well as from hydrogen gas produced by cracking methane. Many industrial processes require pure hydrogen free of acidic gases. Diethanolamine is used to remove troublesome hydrogen sulfide from sour natural gas in transmission lines and natural gasoline plants. It is also used as a softening, moistening, and emulsifying agent; and in the synthesis of organic compounds by esterification of its hydroxyl groups.

It is an excellent agent for neutralizing the acidity which is developed by the high percentage of clays used in rubber compounding, and thus reduces the curing time considerably. It is also used in the production of powerful synthetic detergents and in certain synthetic resins."

Color and properties: Faintly colored, viscous liquid.

Constants: Sp.gr. 1.0985 at 20°C./20°C.; b. p. (760 mm.) 268.0°C.; vapor pressure < 0.01 mm. (20°C.); flash point 280°F.; wt. 91. lbs./gal. (20°C.). *Typical specifications:* Sp.gr. 1.088 to 1.095 at 30°C./20°C.; water not more than 1.5%; monoethanolamine not more than 2%; diethanolamine not less than 95%; triethanolamine not more than 2%; color (100-mm. tube) not more than 3 yellow and 1 red Lovibond; equivalent wt. 104 to 108; average wt. 9.08 lbs./gal. (30°C.).

Miscible with water and most organic solvents.

Triethanolamine [Tri-2-hydroxyethylamine $(HOCH_2CH_2)_3N$].[4] "Triethanolamine is a viscous and very hygroscopic liquid with a slight ammoniacal odor. It boils at 244°C at 50 mm. (360°C at 760 mm) and is entirely soluble in water and alcohols but only slightly soluble in hydrocarbons. It is a mild, organic base which like ammonia, combines with acids and acidic materials. The alkalinity of pure triethanolamine is somewhat less than that of ammonia, its pH being 11.2 in 25 per cent solution.

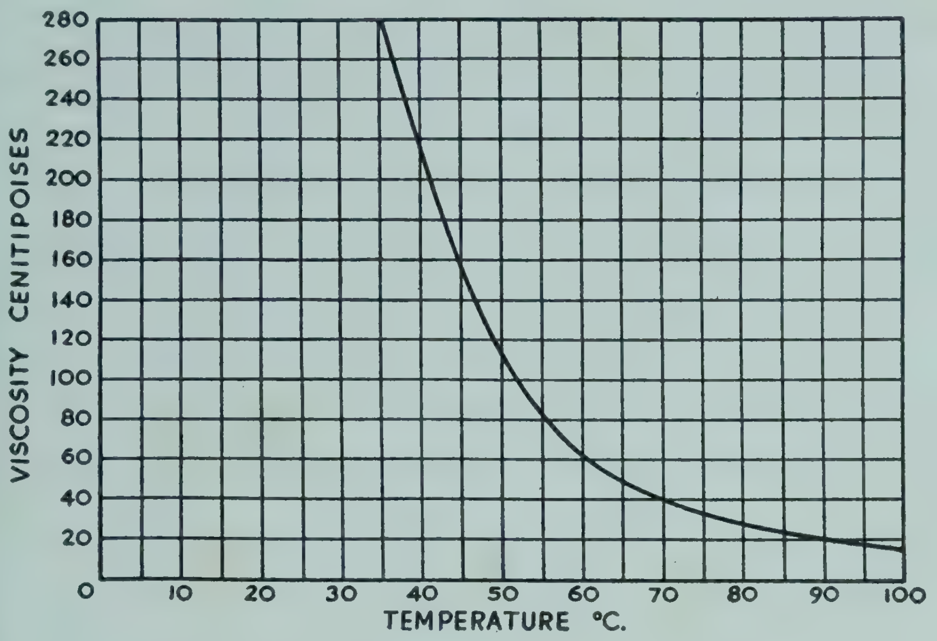


Figure 10-20. Viscosity of Triethanolamine at Various Temperatures.

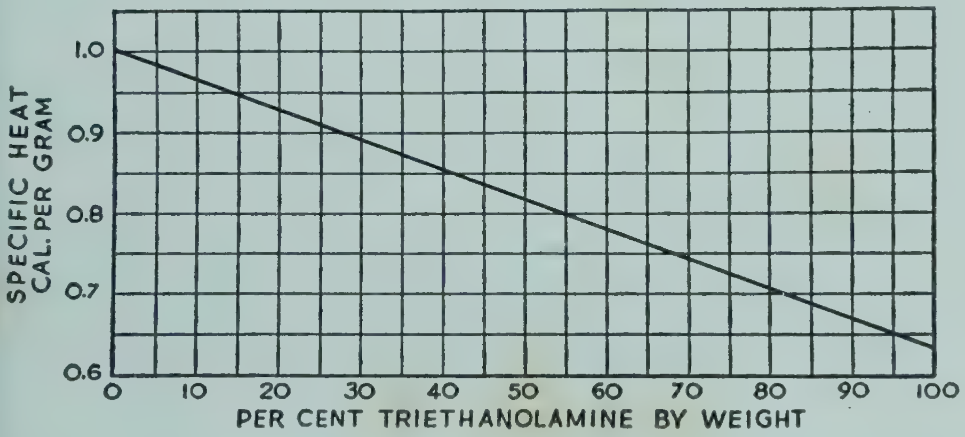


Figure 10-21. Specific Heats of Aqueous Triethanolamine Solutions at 21°C.[4]

"Three commercial grades of triethanolamine are available: 98 per cent, "regular" and "SP." These differ only slightly in physical and chemical properties from the pure compound. The most significant variation is in equivalent weights. Pure Triethanolamine has an equivalent weight of 149; "regular", 140; and "SP", about 130. This variation is due to increasing amounts of mono- and diethanolamine present in the respective commercial grades.

"With free fatty acids, triethanolamine forms soaps in direct molecular proportions. Triethanolamine oleate is a semi-liquid soap capable of forming solutions of marked detergent properties in water or in organic solvents such as gasoline. In water, triethanolamine oleate is soluble in all proportions; in gasoline, more than 2 per cent soap is necessary to effect solution.

The stearate is a hard, white product which finds use in cosmetic preparations. Only the 98 per cent or regular grades should be used in cosmetic products. These soaps are practically neutral, their pH being approximately 8, and are thus free from irritating effect upon the skin or from injurious effect on fabrics. Very stable water emulsions of almost any oil, fat, or wax can in general be prepared with these soaps. The usual requirements for emulsification are between 2 and 4 per cent triethanolamine and 5 to 15 per cent oleic or stearic acid, each based on the weight of the oil to be emulsified. Triethanolamine emulsions are distinguished by their small particle size, non-corrosiveness, non-volatility, ease of preparation, and wide flexibility in formulation without fear of separation."

A small percentage of triethanolamine assists in the penetration of liquids into porous materials. Because of its pronounced hygroscopicity, it is employed as an economical softening agent, humectant, and plasticizing agent for such products as textiles, glues, leather coatings, as a penetrating agent in impregnating wood, paper, and cellulose products. Also an ingredient of adhesives, rubber mixtures and lacquers.

Typical Properties and Specifications

Viscous, pale yellow liquid intermediate in properties between alcohol and ammonia; slightly ammoniacal odor; excellent penetrating properties; forms soaps with fatty acids; hygroscopic. Commercial product contains 70–75% triethanolamine, 20–25% diethanolamine, 0–5% monoethanolamine. Soluble in water, alcohol and chloroform. Sp.gr. 1.1204–1.1284; b.p. 360°C; vapor pressure < 0.01 mm (20°C); flash point 355°F; wt./gal. 9.4 lbs. (20°C); coefficient of expansion 0.00048 (20°C); freezing point 21.2°C; viscosity 0.10 poise (20°C).

Typical specifications: Sp. gr. 1.1240–1.1300 (20/20°C); water not more than 1.0%; purity not more than 2.5% monoethanolamine, not more than 15% diethanolamine, not less than 80% triethanolamine; equivalent wt. 140–145; color (500-mm. tube) not more than 7 yellow and 2 red Lovibond; average wt./gal. 9.40 lbs. (20°C).

Isopropanolamines (Mixed). The mixed isopropanolamines are available as a liquid mixture of mono-, di-, and triisopropanolamine.

Uses: The isopropanolamine soaps may be employed in all uses now found for the ethanolamine soaps. Their excellent hydrocarbon solubility and color stability makes them of special interest in soluble oils, dry cleaning soaps, cosmetics, and pharmaceutical preparations. Vinyl acetate resin emulsions of the oil-in-water type for coating fabrics and leather have excellent stability when prepared by stirring 80 parts by weight of "Vinylite" resin AYAF (30 per cent solution in toluene) and 1 part oleic acid into 20 parts of water containing 0.6–0.8 parts of mixed isopropanolamine.

Kerosene solubilized with 4 per cent by weight of mixed isopropanolamine and 15 per cent by weight of oleic acid produces stable emulsions with water upon mechanical agitation. Stable water emulsions of chlorinated hydrocarbons or naphtha may be prepared by a similar procedure.

The addition of about 2 per cent by weight of mixed isopropanolamine has been found to improve the penetration of starch glues into heavily sized envelope stock.

Purity	
Monoisopropanolamine	14± 2% by wt.
Diisopropanolamine	43± 4% by wt.
Triisopropanolamine	43+ 4% by wt.
Specific gravity at 20/20°C	1.0040–1.0100

Triisopropanolamine. [Tri-2-hydroxyisopropylamine, $(CH_3CHOHCH_2)_3N$]. This compound is a white, crystalline solid, completely soluble in water. It is used as a reactant in pharmaceutical syntheses. It is important in the oral treatment of syphilis. Combined with sodium bismuthate and propylene glycol, it produces a bismuth compound stable enough to withstand chemical action of the digestive system. Triisopropanolamine can be used for the preparation of cosmetic creams, "soluble" oils, and emulsions—where the good color stability of its soaps is of interest. Formulas containing lanolin may vary in color stability. Triisopropanolamine is especially suggested for "soluble" white paraffin oils for the rayon industry, where good color and a low free fatty acid content are desirable.

Boiling point (760 mm)	305.4°C
Flash point	305°F
Latent heat of vaporization	45°C
Melting point	46°C
pH 25% Solution at 25°C	10.7
Equivalent weight	188–192
Specific gravity at 50/20°C	0.9996
Solubility in water at 20°C	Complete
Solubility of water in amine	Complete
Vapor pressure at 20°C	0.01 mm Hg
Weight per gallon at 50°C	8.32 lbs.

2-Amino-2-methyl-1-propanol [$CH_3C(CH_3)NH_2CH_2OH$].

This is a water-white, syrupy, alkaline liquid, with a faint ammoniacal odor and is soluble in water and many organic solvents. It forms soaps with higher fatty acids and these are useful as emulsifying agents in textile and leather materials, water-emulsion paints, and self-polishing waxes.

Boiling point (760 mm)	165°C
Melting point	25°C
Specificity gravity	0.934
pH (0.1 *M* solution at 20°C	11.27
Solubility in 100 cc water	Complete
Vapor pressure at 20°C	1.0 mm
Flash point (Tag. open cup)	153°F
Refractive index at 20°C	1.449
Weight per Gallon at 68°F	7.77 lbs

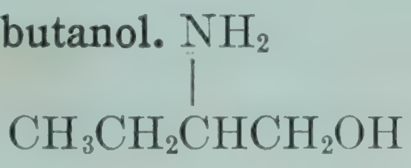
2-Amino-2-methyl-1,3-propanediol [$CH_2OHC(CH_3)NH_2CH_2OH$].

Boiling point at 10 mm	151°C
Melting point	109–111°C
pH (0.1 *M* solution) at 20°C	10.78
Solubility in 100 cc water	250 grams

2-Amino-2-ethyl-1,3-propanediol [$CH_2OHC(C_2H_5)NH_2CH_2OH$].

Boiling point at 10 mm	153°C
Flash point (Tag. open cup)	166°F
Melting point	37.5 to 38.5°C
pH of 0.17 *M* aqueous solution at 20°C	10.8
Solubility in water at 20°C	Complete
Specific gravity at 20/20°C	1.099
Refractive index at 20°C	1.490
Weight per gallon at 68°F	9.15 lbs.

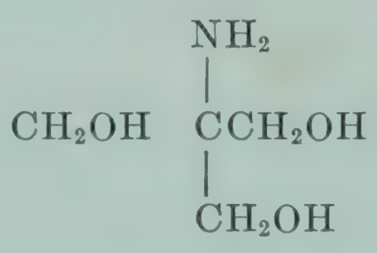
2-Amino-1-butanol.



$CH_3CH_2\overset{\overset{NH_2}{|}}{C}HCH_2OH$

Boiling point at 760 mm	178°C
Flash point (Tag. open cup)	164°F
Melting point	−2°C
pH of 0.1*M* aqueous solution at 20°C	11.1
Specific gravity at 20°/20°C	0.944
Solubility in water at 20°C	Completely Miscible
Vapor pressure at 20°C (est)	0.5 mm
Refractive index at 20°C	1.453

Tris (hydroxymethyl) aminoethane



$CH_2OH\ \underset{\underset{CH_2OH}{|}}{\overset{\overset{NH_2}{|}}{C}}CH_2OH$

Boiling point at 10 mm	219 to 220°C
Melting point	171 to 172°C
pH of 0.1*M* aqueous solution at 20°C	10.4
Solubility in water at 20°C	80 grams per 100 ml

2-Aminoethylethanolamine (Hydroxyethyl ethylenediamine, $NH_2CH_2CH_2NHCH_2CH_2OH$). This compound is a hygroscopic liquid with a mild ammoniacal odor; it is completely soluble in water. It is used in the manufacture of dyes, pharmaceuticals, textile specialties, flotation agents, resins, insecticides and rubber products.

Boiling point at 760 mm	243.7°C
Flash point	275°C
Specific gravity at 20/20°C	1.0304
Solubility in water	Complete
Solubility of water in solvent	Complete
Vapor pressure at 20°C	0.02 mm Hg
Weight per gallon at 20°C	8.58 lbs.
Boiling range at 760 mm	232–250°C
Purity	99%, min

1-Diethylamino-2,3-propanediol [$(C_2H_5)_2NCH_2CHOHCH_2OH$]. This alkylol amine is a water-white to light-straw liquid with a faintly ammoniacal odor. It is soluble in water, methyl alcohol, ethyl ether, ethyl acetate, acetone, aromatic hydrocarbons, fixed oils, oleic and hot stearic acids and hot carnauba wax, the latter solidifying when cooled. It is insoluble in mineral oil and paraffin wax.

Boiling range	233–235°C
Flash point	210°F
Specific gravity at 20/20°C	0.973

ALKYLALKANOLAMINES

This group of compounds, also referred to as alkylaminoethanols, have less odor than most alkylamines and possess both water and oil solubility. The solubility degree of each is determined by the number of alkyl or hydroxyl groups present in the molecule. A larger number of hydroxyl groups gives greater water solubility, whereas a predominance of alkyl groups gives greater oil solubility. The derivatives of these compounds are of particular interest. They form soaps with fatty acids which may be employed as emulsifying, penetrating and wetting agents, and these uses can also be applied to the ester and acid amide derivatives. These amines also serve as intermediates in the manufacture of drugs and dyes.

Sharples Chemicals, Inc.[7] has prepared a tabulation of some of the physical properties of alkylaminoethanols. Several of these compounds are at present being made in commercial quantities.

Ethyl monoethanolamine ($C_2H_5NHCH_2CH_2OH$). This alkylolamine is a colorless liquid, with an amine odor. It is soluble in water, ethyl alcohol, methyl alcohol, ethyl ether, ethyl acetate, acetone, aromatic hydrocarbons, fixed oils, mineral oil, oleic and stearic acids, and hot carnauba and paraffin waxes, the latter two solidifying when cooled. It is only slightly soluble in paraffinic hydrocarbons. (For properties see Table 10.6.)

Ethyl diethanolamine [$C_2H_5N(CH_2CH_2OH)_2$]. Ethyl diethanolamine is a water-white liquid with an amine odor and soluble in water, ethyl alcohol, methyl alcohol, acetone, aromatic hydrocarbons, some fixed oils, oleic and hot stearic acids. It is insoluble in linseed and cottonseed oils, mineral oil, paraffin and carnauba waxes. It is only slightly soluble in paraffinic hydrocarbons. (For properties see Table 10.6)

***n*-Butyl monoethanolamine** ($C_4H_9NHCH_2CH_2OH$). This alkylol amine is a water-white liquid with a faintly amine odor. It is soluble in water, ethyl alcohol, methyl alcohol, ethyl ether, ethyl acetate, acetone, aromatic hydrocarbons, fixed oils, oleic and stearic acids, and hot carnauba and paraffin waxes, the latter two solidifying when cooled. It is only slightly soluble in paraffinic hydrocarbons. (See properties in Table 10.6.)

TABLE 10.6. *Alkylaminoethanols*[7]

	Diethylamino-ethanol	Ethyl Monoethanolamine	Ethyl Diethanolamine
Color	Water-white	Water-white	Water-white
Specific gravity at 20°/20°C.	0.88–0.89	0.92	1.02
Minimum amine content	99.5%	98.5%	98.5%
Initial boiling point	158°C.	161°C	245°C.
Final boiling point	163°C.	174.5°C.	260°C.
Flash point	135°F.	160°F.	255°F.
Solidification point	<−70°C.	−8.8°C.	−50°C.
Refractive index at 20°C.	1.440	1.444	1.466
Viscosity at 25°C (centipoise)	4.05	12.40	53
Viscosity at 60°C (centipoise)	1.50	3.22	11.2
*Coefficient of expansion per °C.	0.0012	0.00091	0.00080
Theoretical molecular weight	117.19	89.14	133.19
Average weight per gallon	7.36 lbs.	7.66 lbs.	8.5 lbs.

	Di-n-Butyl-aminoethanol	n-Butyl-Monoethanolamine	n-Butyl Diethanolamine
Color	Water-white	Water-white	Water-white to Light Straw
Specific gravity at 20°/20°C.	0.860	0.89	0.97
Minimum amine content	98.5%	96.0%	95.0%
Initial boiling point	222°C.	192°C.	262°C.
Final boiling point	234°C.	215°C.	290°C.
Flash point	200°F.	170°F.	245°F.
Solidification point	<−70°C.	−3.5°C.	<−70°C.
Refractive index at 20°C.	1.444	1.444	1.462
Viscosity at 25°C (centipoise)	6.50	17.4	55
Viscosity at 60°C (centipoise)	1.94	4.02	10.6
*Coefficient of expansion per °C.	0.00114	0.0010	0.00077
Theoretical molecular weight	173.29	117.19	161.24
Average weight per gallon	7.16 lbs.	7.44 lbs.	7.25 lbs.

Dimethylethanolamine [$(CH_3)_2NCH_2CH_2OH$]. Dimethylethanolamine is a water-white liquid with an amine odor. It resembles diethylethanolamine in chemical behavior and it is used as an intermediate in the synthesis of corrosion inhibitors, dyes, pharmaceuticals, and textile auxiliaries.

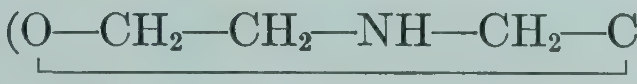
Boiling point	133°C
Equivalent weight	89
Specific Gravity at 20/20°C	0.887
Refractive index	1.4300

Diethylethanolamine (Diethylaminoethanol, $(C_2H_5)_2NC_2H_4OH$). Diethylaminoethanol is a water-white, hygroscopic liquid which behaves chemically like the tertiary amines and alcohols. It is soluble in water, ethyl alcohol, methyl alcohol, ethyl ether, ethyl acetate, acetone, aromatic hydrocarbons, fixed oils, mineral oil, oleic acid, hot stearic acid, and hot paraffin and carnauba waxes, the last two solidifying when cooled. It is used in the manufacture of certain pharmaceuticals, such as procaine and "atabrine". It forms amine soaps with higher fatty acids, which are oil-soluble and useful as emulsifiers and textile lubricants. Its mild alkalinity makes it applicable as a neutralizing agent and a corrosion inhibitor. (For properties, see Table 10.6.)

Di-n-butylethanolamine (Di-*n*-Butylaminoethanol, $(C_4H_9)_2NCH_2CH_2OH$). This alkylolamine is a water-white liquid with a faintly amine odor. It is insoluble in water but soluble in ethyl alcohol, methyl alcohol, ethyl ether, ethyl acetate, aromatic hydrocarbons, fixed oils, mineral oil, oleic and hot stearic acids, and hot paraffin and carnauba waxes, the latter two solidifying when cooled. It is slightly soluble in paraffinic hydrocarbons. (For properties, see Table 10.6.)

n-Butyl diethanolamine $[C_4H_9N(CH_2CH_2OH)_2]$. This alkylol amine is a light straw-colored liquid with a faintly amine odor. It is soluble in water, ethyl alcohol, methyl alcohol, ethyl ether, ethyl acetate, acetone, aromatic hydrocarbons, castor oil, oleic and hot stearic acids, and hot carnauba wax, the latter solidifying when cooled. It is insoluble in linseed and cottonseed oils, mineral oil, and paraffin wax. (For properties see Table 10.6.)

MISCELLANEOUS AMINES



Morpholine ($O\text{—}CH_2\text{—}CH_2\text{—}NH\text{—}CH_2\text{—}CH_2$). This commercially important secondary amine is a water-white, mobile liquid having an ammoniacal odor. It is very soluble in water and forms a stable solution which exhibits a constant composition during evaporation and distillation as well as preserving a constant alkalinity. The ring structure of this solvent, as well as its ether and amine groups, gives it unique solvent power for a greater than usual variety of organic substances, among which are resins, dyes, waxes, shellac, and casein.

It is used in permanent wave solutions for its mild alkalinity; in soaps which are emulsifying agents for paper coatings; in rubless polishes, lacquers, paints, insecticides, etc. It imparts water-resistance after drying. Its water-soluble salts have high phenol coefficients. Morpholine may also be used in photographic developing.

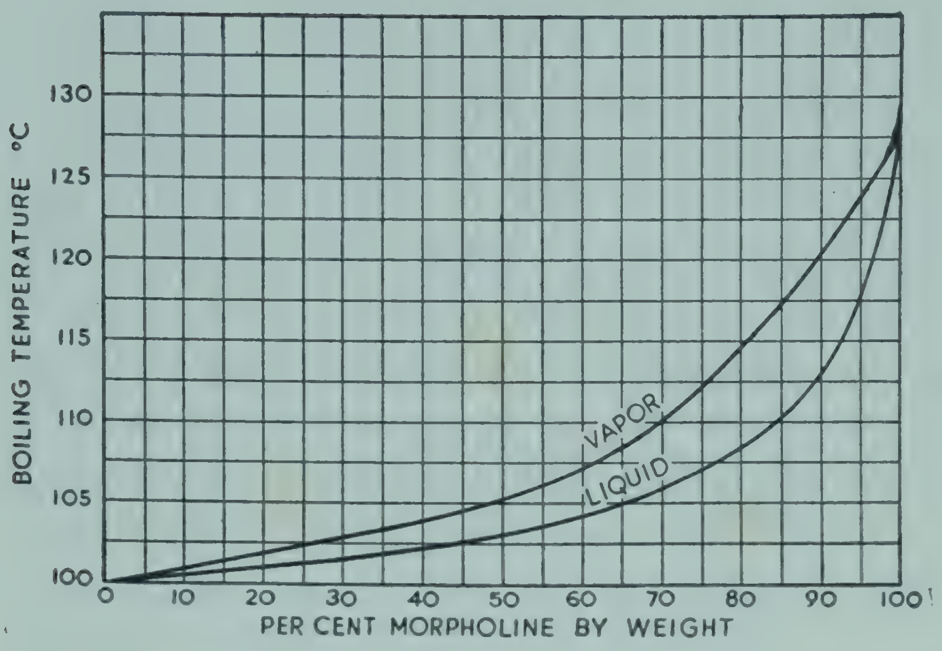


Figure 10-22. Boiling-Point Composition Curves for Aqueous Morpholine Solutions.[4]

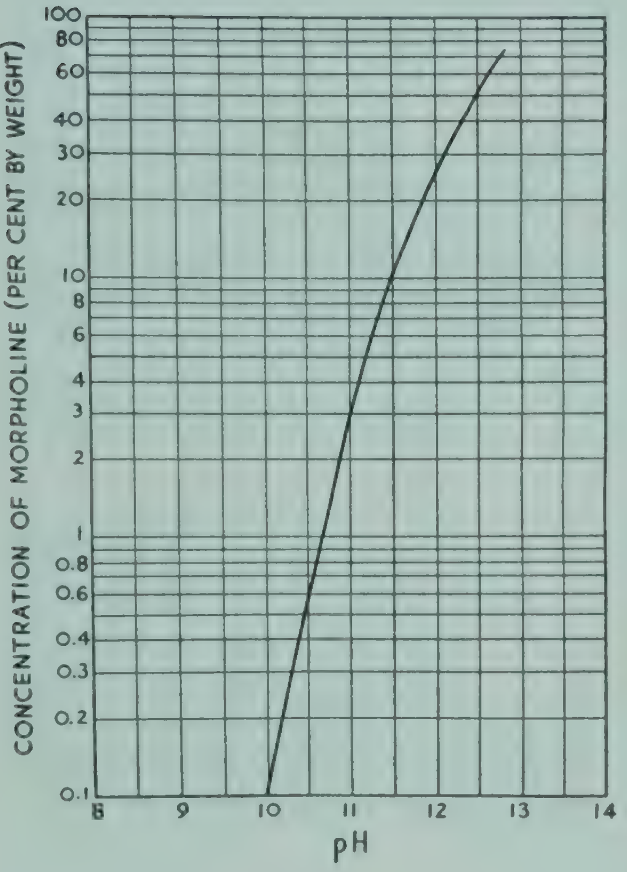


Figure 10-23. pH of Aqueous Morpholine Solutions at 25°C.[4]

Typical Properties and Specifications

Boiling Point	128.9°C
Color	Water-white
Flash point (open cup)	100°F
pH of 25% solution at 25°C	11.4
Specific gravity at 20/20°C	1.0017
Solubility in water at 20°C	Complete
Solubility of water in solvent at 20°C	Complete
Vapor pressure at 20°C	8.0 mm
Weight per gallon at 20°C	8.34 lbs.
Ash	0.05 g. per 100 cc. (max.)
Boiling Range at 760 mm	Below 120°C None Above 132°C None
Purity	98% (min.)

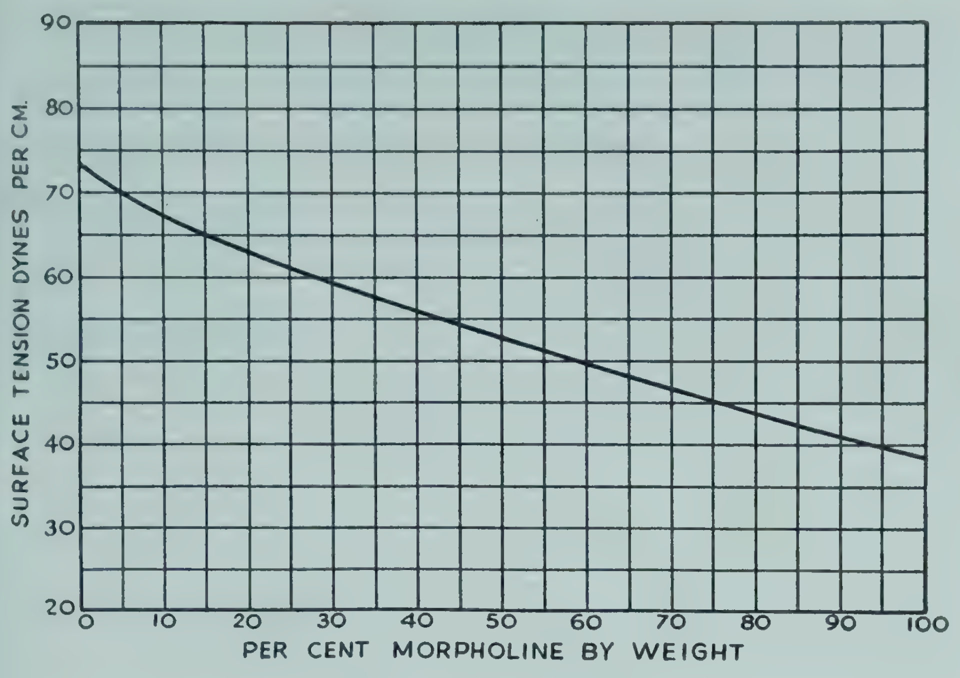


Figure 10-24. Surface Tension of Aqueous Morpholine Solutions at 20°C.[4]

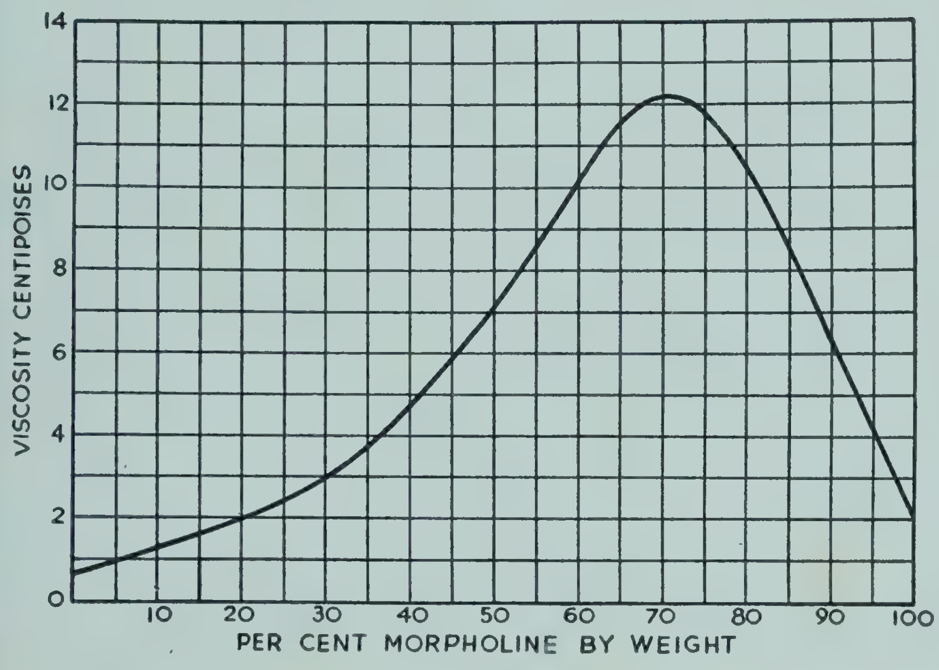
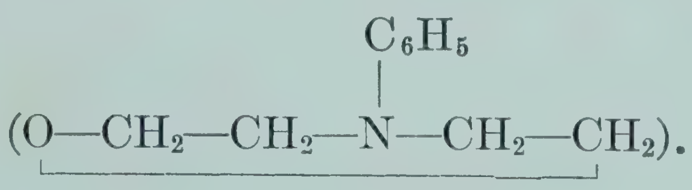


Figure 10-25. Viscosity of Aqueous Morpholine Solutions at 20°C.[4]

n-Ethyl morpholine ($C_2H_5N—CH_2—CH_2—O—CH_2—CH_2$). This cyclic tertiary amine is a water-white liquid miscible with water. It may be used as a solvent for oils, dyes, and resins and as an intermediate in the synthesis of rubber accelerators, emulsifying agents, drugs, and dyes.

Boiling point	138°C
Specific gravity at 20/20°C	0.916

Phenyl morpholine



$$(O—CH_2—CH_2—\overset{\overset{C_6H_5}{|}}{N}—CH_2—CH_2).$$

Boiling point at 760 mm	268°C
Melting point	57°C

Tetraethanolammonium hydroxide [$N(C_2H_4OH)_4OH$]. This solvent is a white, crystalline, strongly basic solid, completely miscible with water. The commercial product is an aqueous methanol solution in which 40 to 41 per cent of this solvent is present. Although aqueous solutions of this solvent are stable at ordinary temperatures, it will decompose when heated to weakly basic tertiary amines. This property is utilized in processes where it is desired to destroy a strongly alkaline substance which is no longer needed. Tetraethanolammonium hydroxide is also a good solvent for certain types of dyes.

Color	White
Description	Crystalline solid
Melting point	123°C
Solubility in water	Complete
Solubility of water in solvent	Complete
Vapor pressure at 20°C	0.01 mm

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1. Mann, C. A., Lauer, B. E., and Hulten, C. I., *Ind. Eng. Chem.*, **28**, 159 (1936)
2. Holson, R. W., Hartman, R. J., and Kanning, E. W., *J. Am. Chem. Soc.*, **63**, 2094 (1941).
3. Bergstrom, F. W., Gilkey, W. M., and Lung, P. E., *Ind. Eng. Chem.*, **24**, 57 (1932).
4. Carbide & Carbon Chemicals Corporation, New York, N. Y.
5. Wilson, A. L., *Ind. Eng. Chem.*, **27**, 867 (1935).
6. Dow Chemical Co., Midland, Michigan.
7. Sharples Chemicals, Inc., Wyandotte, Mich.

Chapter 11

Alcohols

The alcohols, one of the most important classes of industrial solvents, are characterized by their hydroxyl (OH) group. They are not only solvents for a large number of substances, but are the starting point in making a host of others. The alcohols can be made to combine with acids to form esters and to unite with aldehydes, yielding acetals; or water can be split off between two molecules and ethers will be formed. The dehydrogenation of alcohols to form ketones and aldehydes is carried out on a large industrial scale.

The lower monohydric alcohols containing one, two, or three carbon atoms, are completely soluble in water, but those of higher carbon content become progressively less so. This is due to the ratios which exist between the carbon and the hydroxyl group content. On the other hand, as their solubility for water decreases, they become better solvents for hydrocarbon-type compounds.

When alcohols are mixed with a true solvent for cellulose derivatives, they become activated to a point where they also acquire solvent properties for these derivatives. The degree to which an alcohol is activated varies considerably. This important property places alcohols among the group of diluents as far as derivatives of cellulose are concerned. The solvent power of the aliphatic alcohol group for cellulose derivatives increases with an increase in molecular weight within the homologous series. By adding an aromatic hydrocarbon an increase in solvency is imparted for ethyl and benzyl cellulose. Beside this acquired property they will also tolerate the addition of certain amounts of non-solvents. Frequently when an alcohol is added to a solution of nitrocellulose, it causes the solution to become gelatinous on standing. However, upon shaking, it becomes fluid again. This phenomenon of gelation and fluidity is known as *thixotropy*.

The evaporation rates of alcohols as a rule are less than those of other solvents of equal boiling points; therefore in using alcohols as nitrocellulose lacquer diluents one should remember that, because they evaporate less rapidly they remain behind, and since they are not true solvents, the solution equilibrium is disturbed. As indicated in Table 11.1 (p. 459) the number of commercially available alcohols has shown a vigorous inrease since 1925.

Methanol (Methyl alcohol, wood alcohol, CH_3OH). Methanol was first discovered by Robert Boyle in 1661, who obtained it in its crude state from the distillation of hardwood. Not knowing its true nature he gave the name of "adiophorus spirit" to this volatile substance. It continued to be confused with ethyl alcohol for the next 151 years before its distinct identity as methanol was recognized by Philip Taylor. However, its composition was not clearly worked out until 22 years later by Dumas and Peligot.

Wood tar, from which Boyle originally discovered methanol, continued to be its principal source of manufacture until very recent times. Over the past 25 years synthetic methanol made from carbon oxides and hydrogen has practically replaced the wood product. An interesting comparison in the production figures of natural and synthetic methanol is given by the 5,100,000 gallons (approx.) of the natural product made in 1947, and the 80 million gallons (approx.) of the synthetic variety produced in the same year.[1]

The word "methyl" is derived from two Greek words meaning wine or spirit of wood, and in characteristic fashion methyl alcohol, or methanol, acquired a large number of names according to the fancy of its originator. Some of these names are carbinol, colonial spirit, Columbian spirit, methyl hydroxide, pyroxylin spirit, wood alcohol, wood naphtha, and wood spirit. The natural product was generally a crude solvent having many impurities and an offensive odor, but the synthetic methanol of today is a water-white liquid of extremely high purity.

There are several commercial grades of methanol ranging in purity from 92 per cent to as high as 99.9 per cent by volume, while the acetone content may vary from a trace to 8 per cent. The presence of acetone is found to be very desirable when the alcohol is used for certain purposes, for example, in paint removers. Methanol made from the distillation of wood and containing such impurities as acetone, methyl acetate, and various oils, is a more powerful solvent than the chemically pure synthetic product. It is entirely miscible with water, alcohols, ketones, esters, halogenated hydrocarbons and many other organic solvents. It is also partly miscible with benzene.

Methanol will dissolve the wide range of organic compounds, among which are acetylene, alkaloids, soaps, natural and synthetic resins, oils, fats, nitrocellulose and ethyl cellulose. The excellent solvency of methanol is attributed to the high ratio of the hydroxyl content as compared with hydrocarbon content. Solutions of alcohol-soluble gums in methanol have lower viscosities than similar solutions in higher aliphatic alcohols.

Although methanol ranks first as an all-round solvent in the aliphatic series of alcohols, its extensive use as an industrial solvent is restricted because of its relatively high toxicity. Though the homologous alcohols are also physiologically active in varying degrees, they are not as volatile.

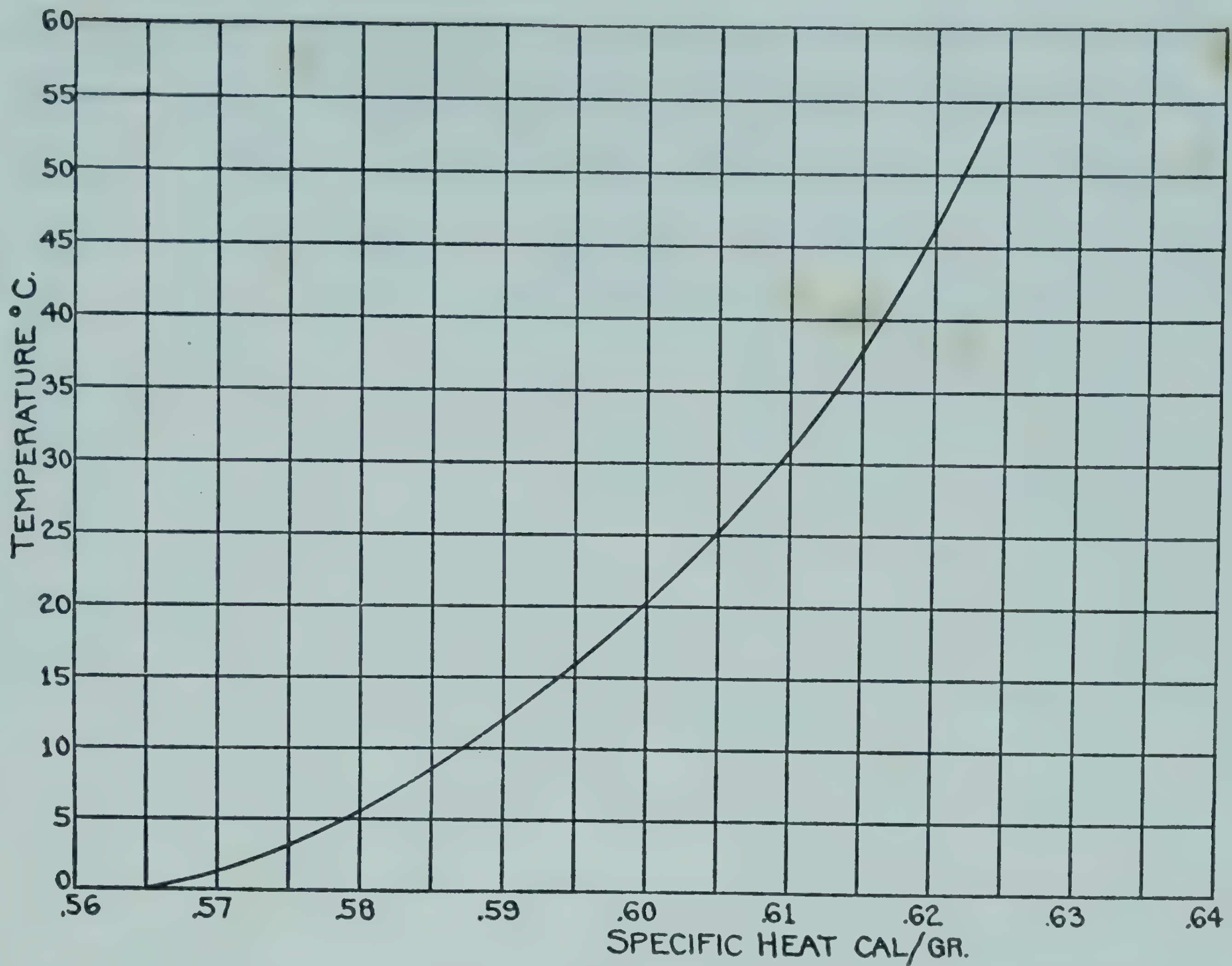

FIGURE 11.1. Specific Heat of Methanol at Various Temperatures.[6]

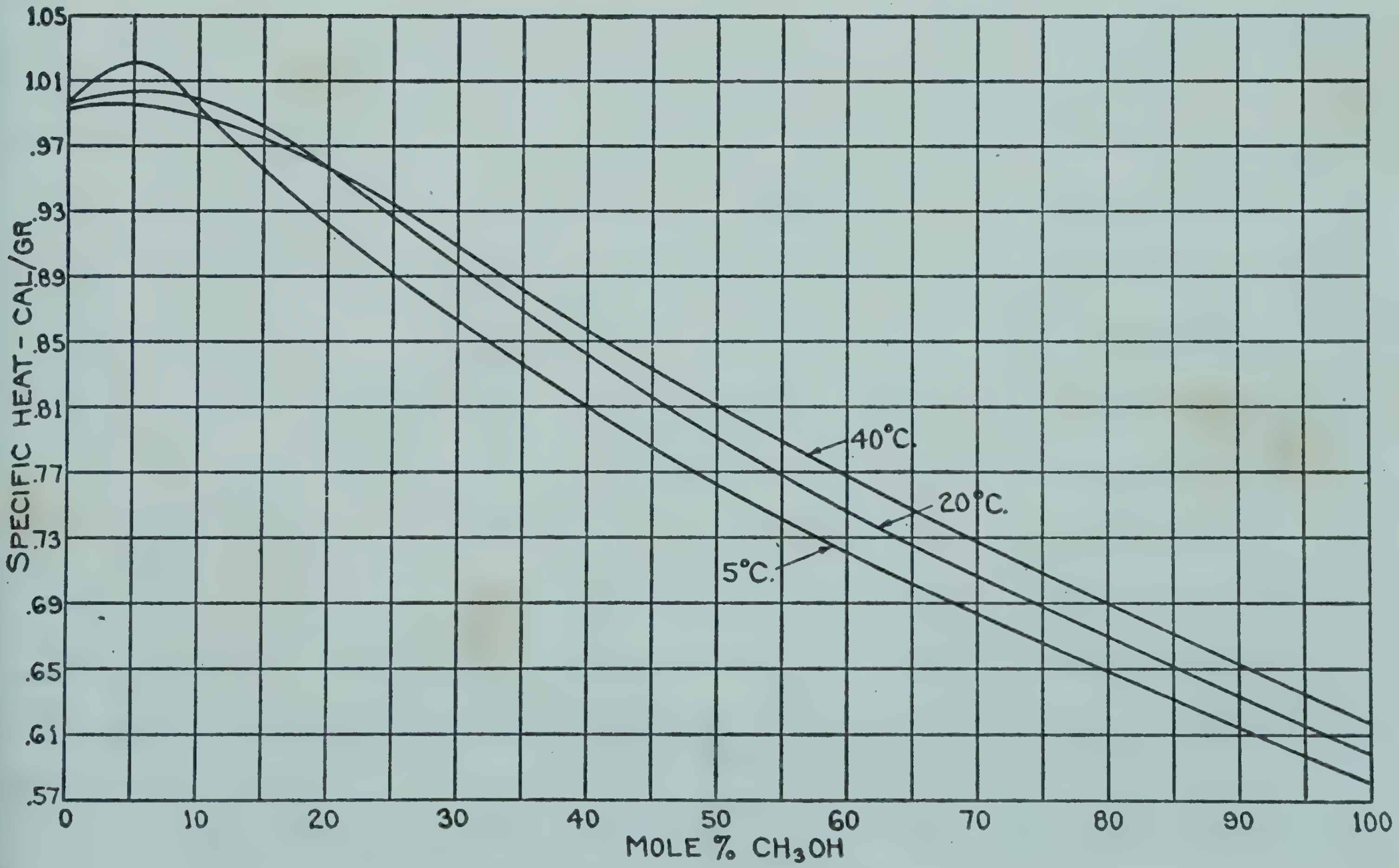

FIGURE 11.2. Specific Heat of Aqueous Solutions of Methanol.[6]

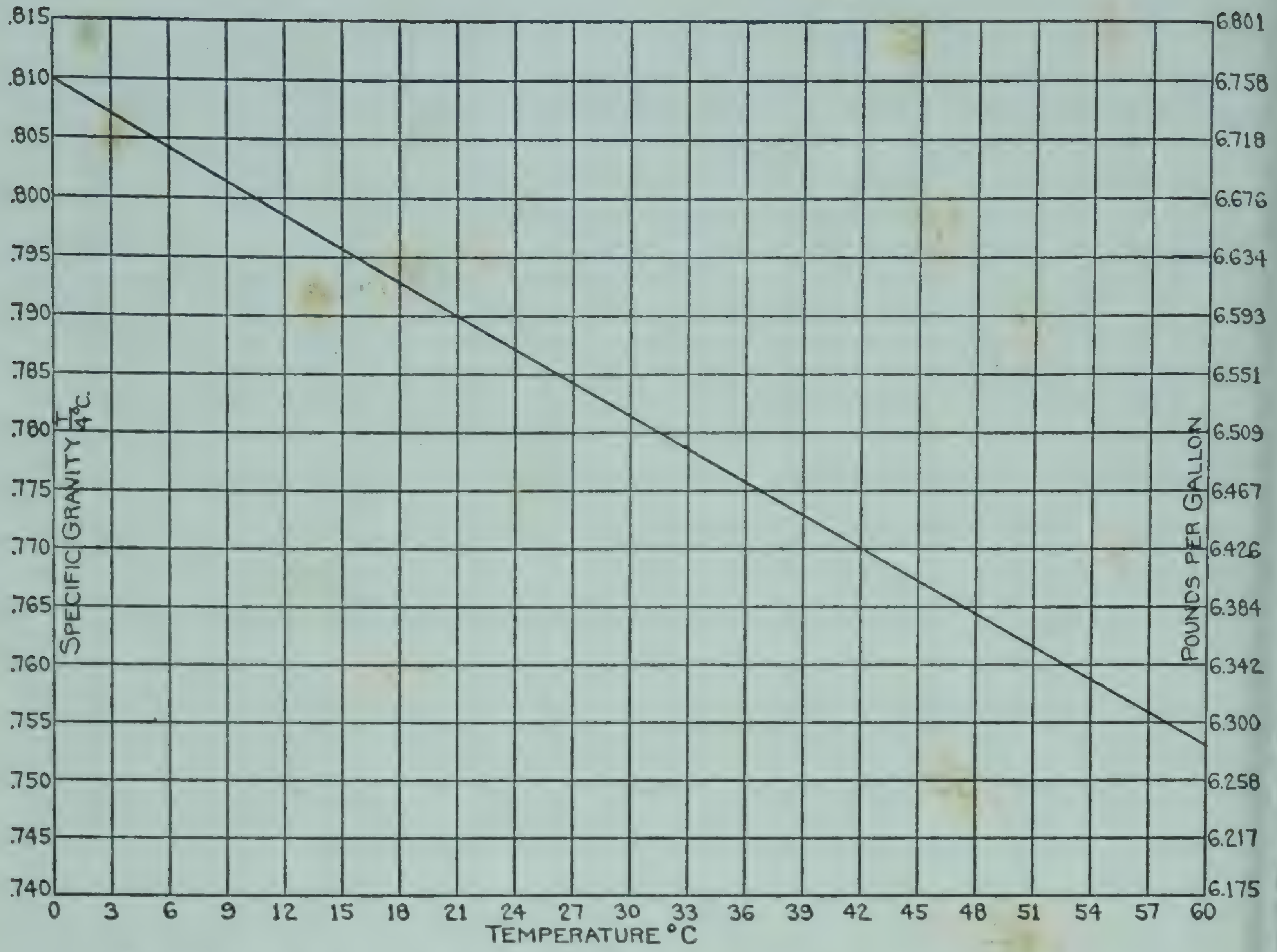

FIGURE 11.3. Specific Gravity and Weight per Gallon of Methanol at Various Temperatures.[6]

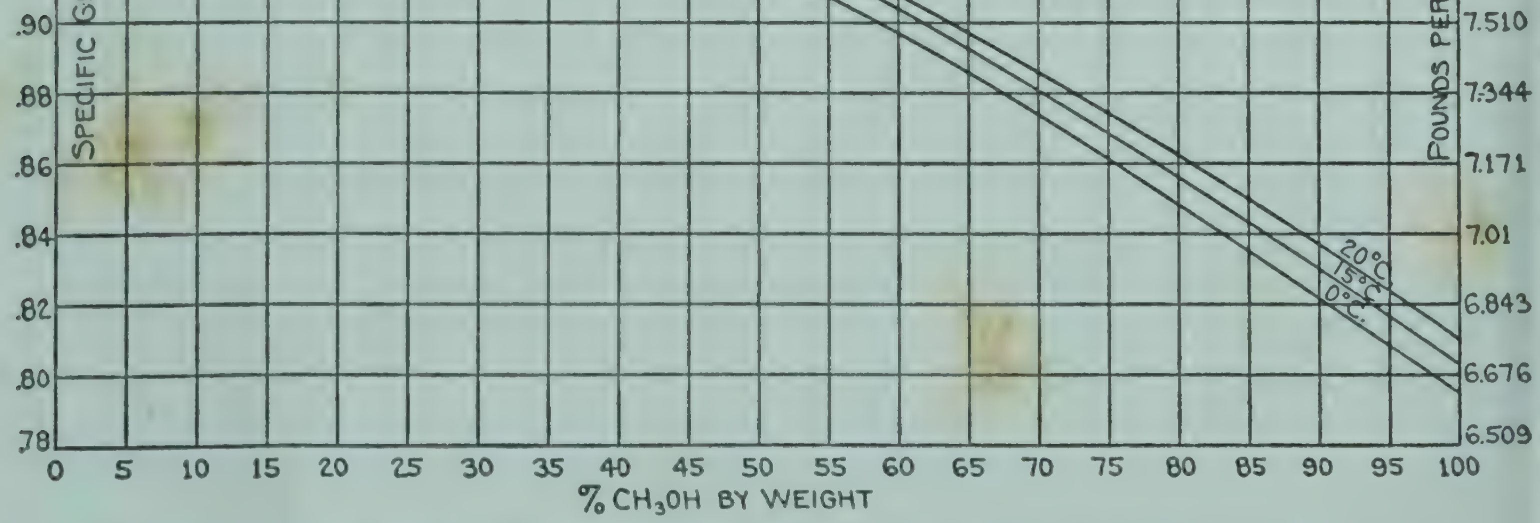

FIGURE 11.4. Specific Gravity and Weight per Gallon of Aqueous Solutions of Methanol.[6]

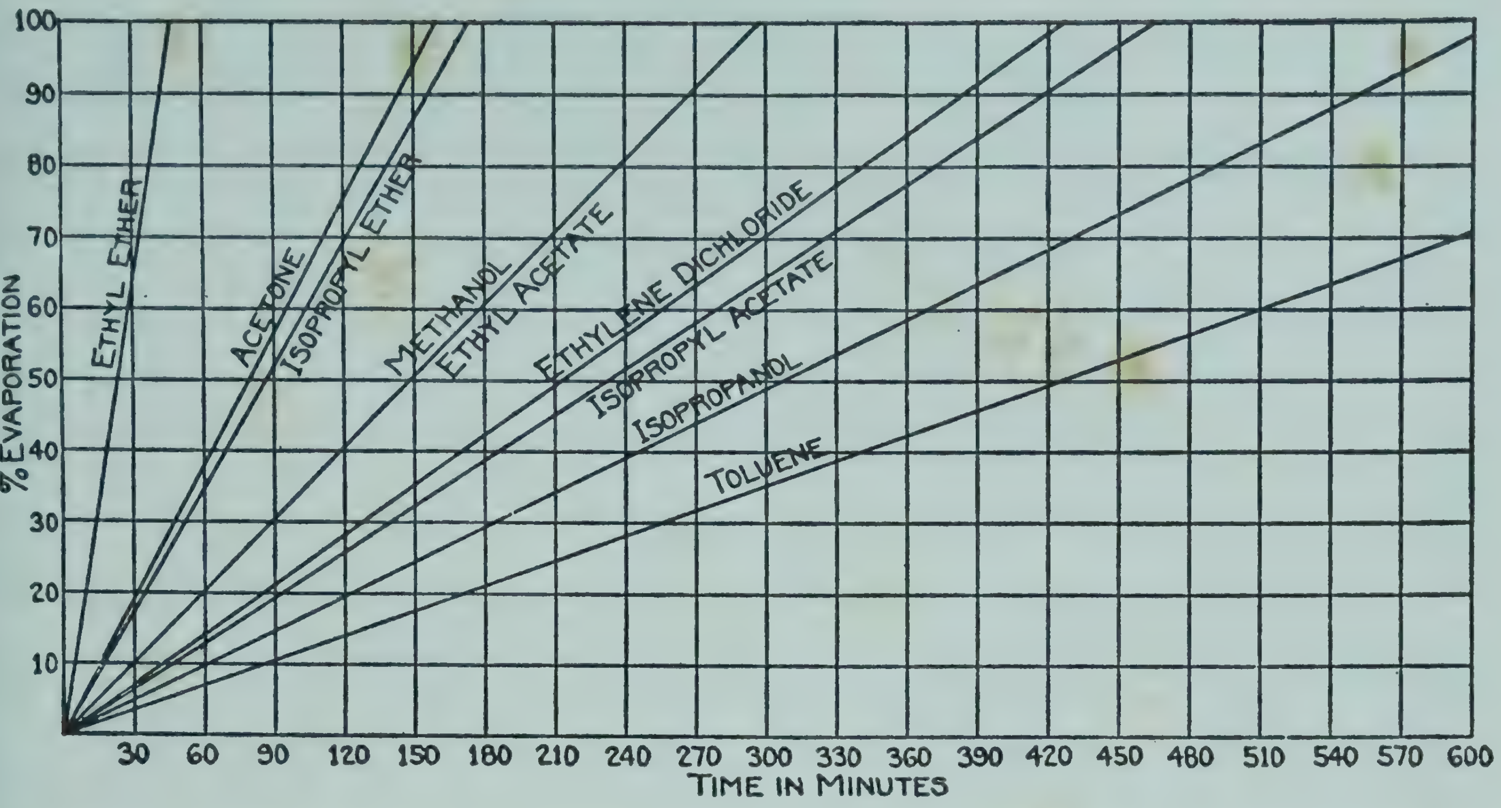

FIGURE 11.5. Evaporation Rate of Various Solvents at Room Temperature.[6]

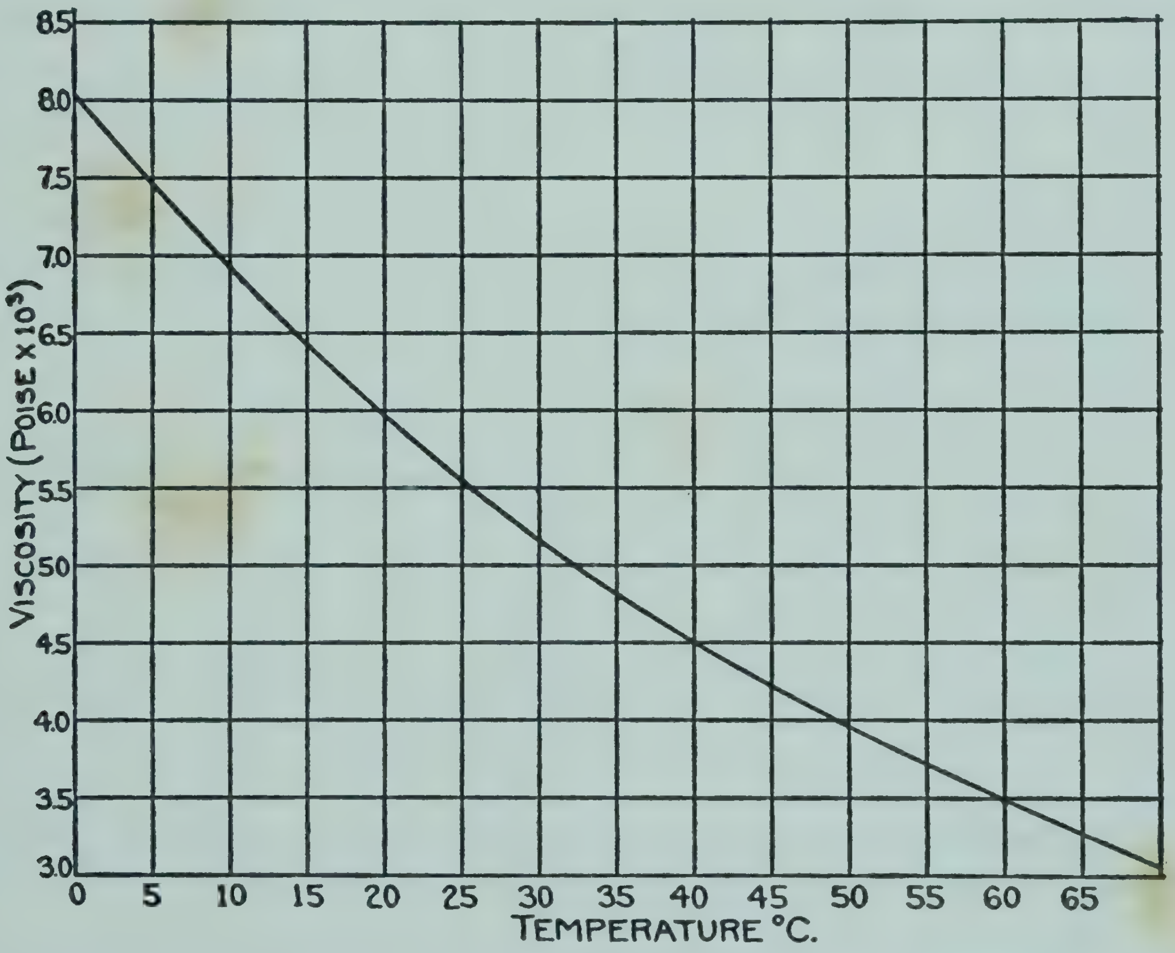

FIGURE 11.6. Viscosity of Methanol at Various Temperatures.[6]

Methanol is used as a solvent in the pharmaceutical industry and in the manufacture of acetate photographic film, plastics, wood stains and paint removers. However, its most important applications are in antifreeze solutions and in the manufacture of formaldehyde. Methyl esters are employed as plasticizers in perfumes and flavors. It is also used as an industrial alcohol denaturant, and in racing fuels.

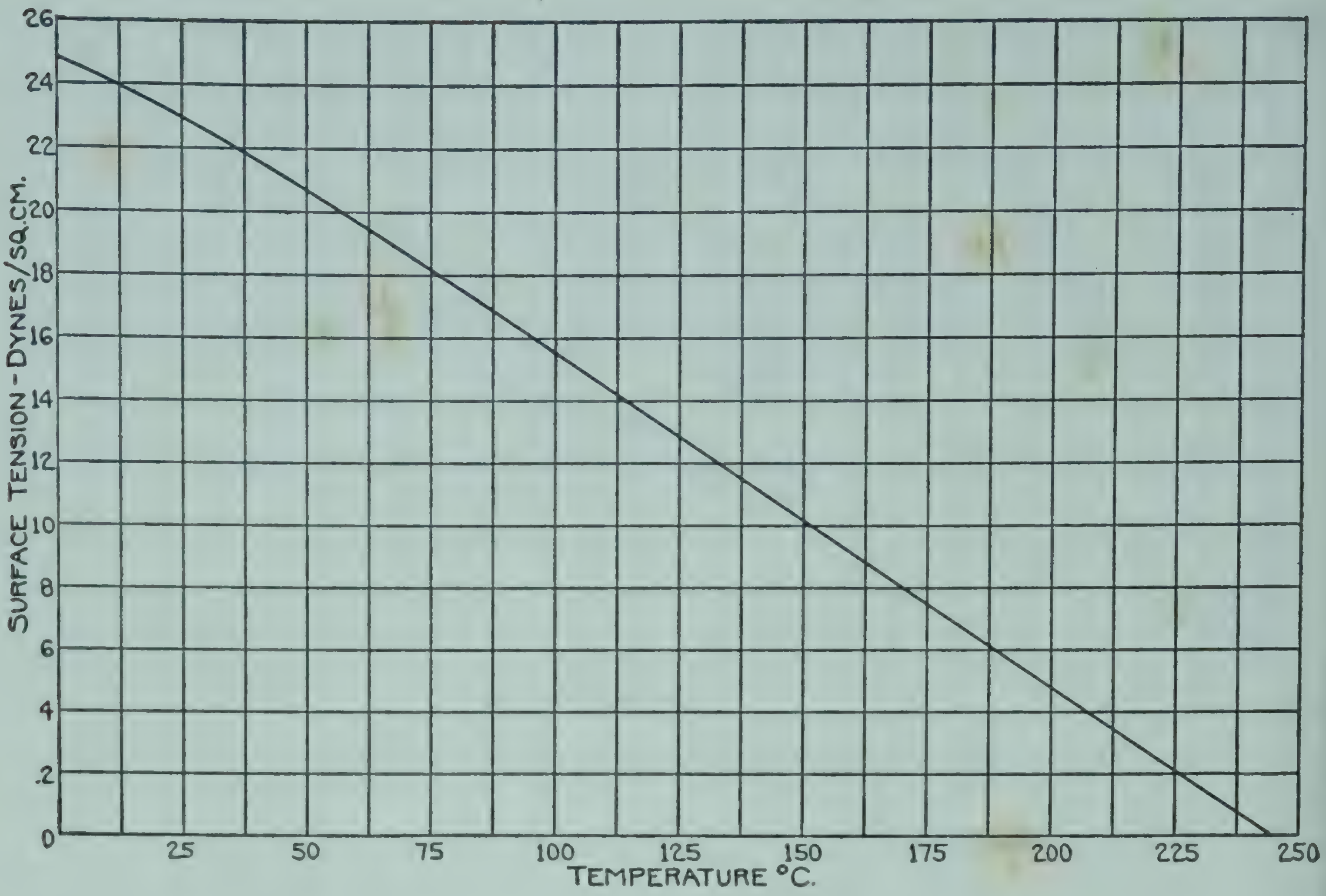

FIGURE 11.7. Surface Tension of Methanol at Various Temperatures.[6]

Complete instructions for the safe handling of methanol are contained in Chemical Safety Data Sheet SD-22 issued by the Manufacturing Chemists' Association (see Chapter 6).

Typical Properties and Specifications

Acidity	0.01% max. calculated as formic acid
Boiling point (at 760 mm)	64.5°C.
Average coefficient of cubical expansion from 0°C to 61°C	0.0012
Critical temperature	240°C
Critical pressure	78.7 atm
Color	Water-white
Dielectric constant at 20°C	31.2
Distillation range	64°–66°C
Electrical conductivity at 18°C	4.4 × 10^{-7} reciprocal ohm.
Flash point	14°C
Heat of combustion	170.9 kg cal./mol.
Heat of fusion	23.6 cal./g.
Latent heat of vaporization at B.P.	262.8 cal./g.
Melting point	−97.8°C
Purity	99.8–99.9%
Specific gravity at 20/4°C	0.792
Specific heat (vapor) at 77°C	0.39 cal./g.
Refractive index at 20°C	1.329
Surface tension at 20°C	22.6 dynes/cm

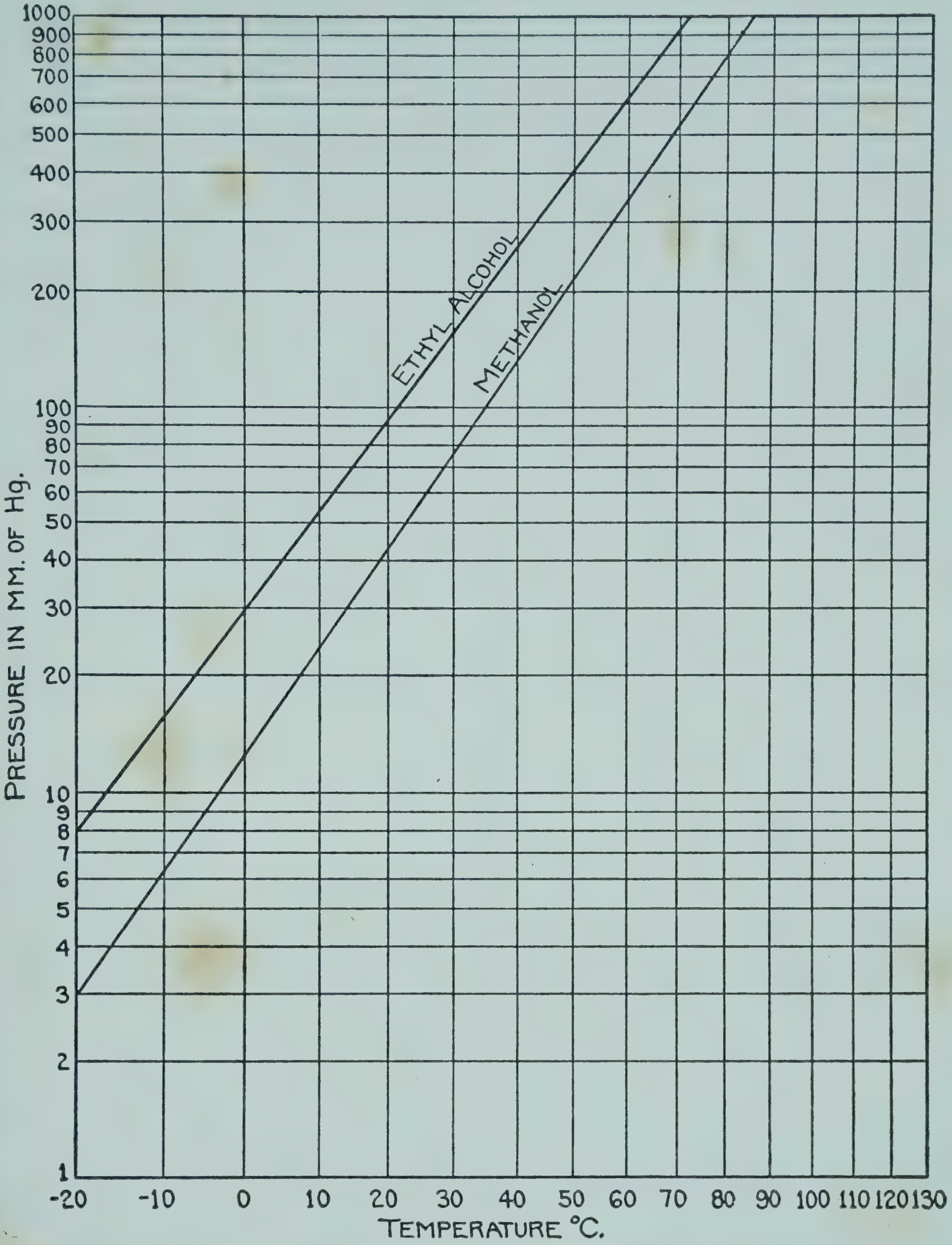

FIGURE 11.8. Vapor Pressure of Ethyl Alcohol and Methanol at Various Temperatures.[6]

Vapor pressure at 0°C	26.6 mm
20	96.0
40	260.5
60	625.0
Viscosity at 20°C	0.00593 poise
Weight per gallon at 20°C	6.59 lbs.

Ethanol (Ethyl alcohol, Cologne spirits, grain alcohol, alcohol) ($CH_3 \cdot CH_2OH$). Until recent years ethanol has been made exclusively by the fermentation of molasses or sugar-forming substances, such as starch and cellulose. It has been made synthetically for over ten years, and the quality of the synthetic product equals that of fermentation ethanol in all respects. Several years ago the U. S. Industrial Chemical Company, Inc. began large-scale manufacture of anhydrous alcohol by azeotropic distillation.

Anhydrous ethanol can be made in a continuous method[2] by adding one of the three dehydration agents, benzene, ethyl ether, or trichloroethylene, which have the property of forming aqueous azeotropes whose boiling points are below that of ethyl alcohol. Thus the aqueous azeotrope is removed as a distillate while the anhydrous product is withdrawn at the bottom of the column. Absolute ethanol can be made on a laboratory scale by the addition of calcium oxide, calcium carbide, or barium oxide and then the removal of the water-free alcohol by distillation.

Azeotropic Mixtures of Ethyl Alcohol

	% by Weight		% by Weight	B.P.(°C)
Ethanol	32.0%	Benzene	68.0	68.2
Ethanol	9.0%	Carbon disulfide	91.0	42.4
Ethanol	15.8%	Carbon tetrachloride	84.2	64.9
Ethanol	7.0%	Chloroform	93.0	59.4
Ethanol	30.5%	Cyclohexane	69.5	64.9
Ethanol	31.0%	Ethyl acetate	69.0	71.8
Ethanol	48.0%	*n*-Heptane	52.0	72.0
Ethanol	21.0%	*n*-Hexane	79.0	58.6
Ethanol	34.0%	Methyl ethyl ketone	66.0	74.8
Ethanol	52.0%	Methyl propionate	48.0	93.2
Ethanol	81.0%	Perchlorethylene	19.0	78.0
Ethanol	68.0%	Toluene	32.0	76.6
Ethanol	27.0%	Trichlorethylene	73.0	70.9

The ethanol of commerce is an azeotropic mixture containing 4.43 per cent water and 95.5 per cent ethanol and boiling at 78.15°C. It is miscible in all proportions with water and many organic solvents, and it is an excellent solvent for many natural products. Anhydrous ethyl alcohol will dissolve sandarac, manila, kauri, pontianac, rosin, wax-free elemi, mastic, dammar, and shellac. It possesses latent solvency for the regular-soluble nitrocellulose and it aids in lowering the viscosity of lacquers. When it is mixed with about 25 per cent hydrocarbons or esters, it will dissolve coumarone resins and ester gum. It is a solvent for phenolic resins, cellulose ethers, and alcohol-soluble nitrocellulose. When combined with an aromatic hydrocarbon or an ester-solvent, solvent power is imparted for an even larger number of resins and cellulose ethers.

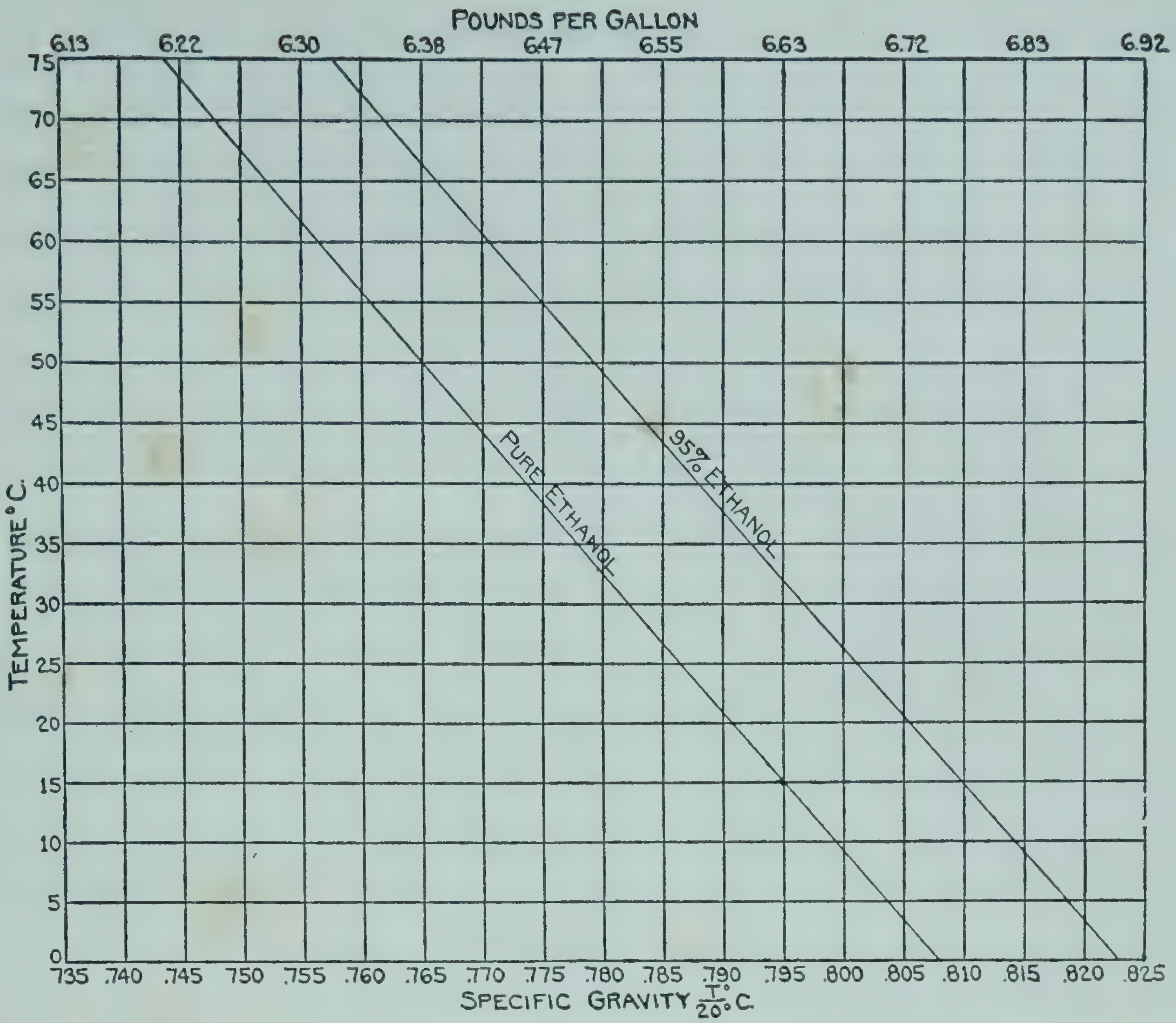

Figure 11.9. Specific Gravity and Weight per Gallon of Ethanol at Various Temperatures.[6]

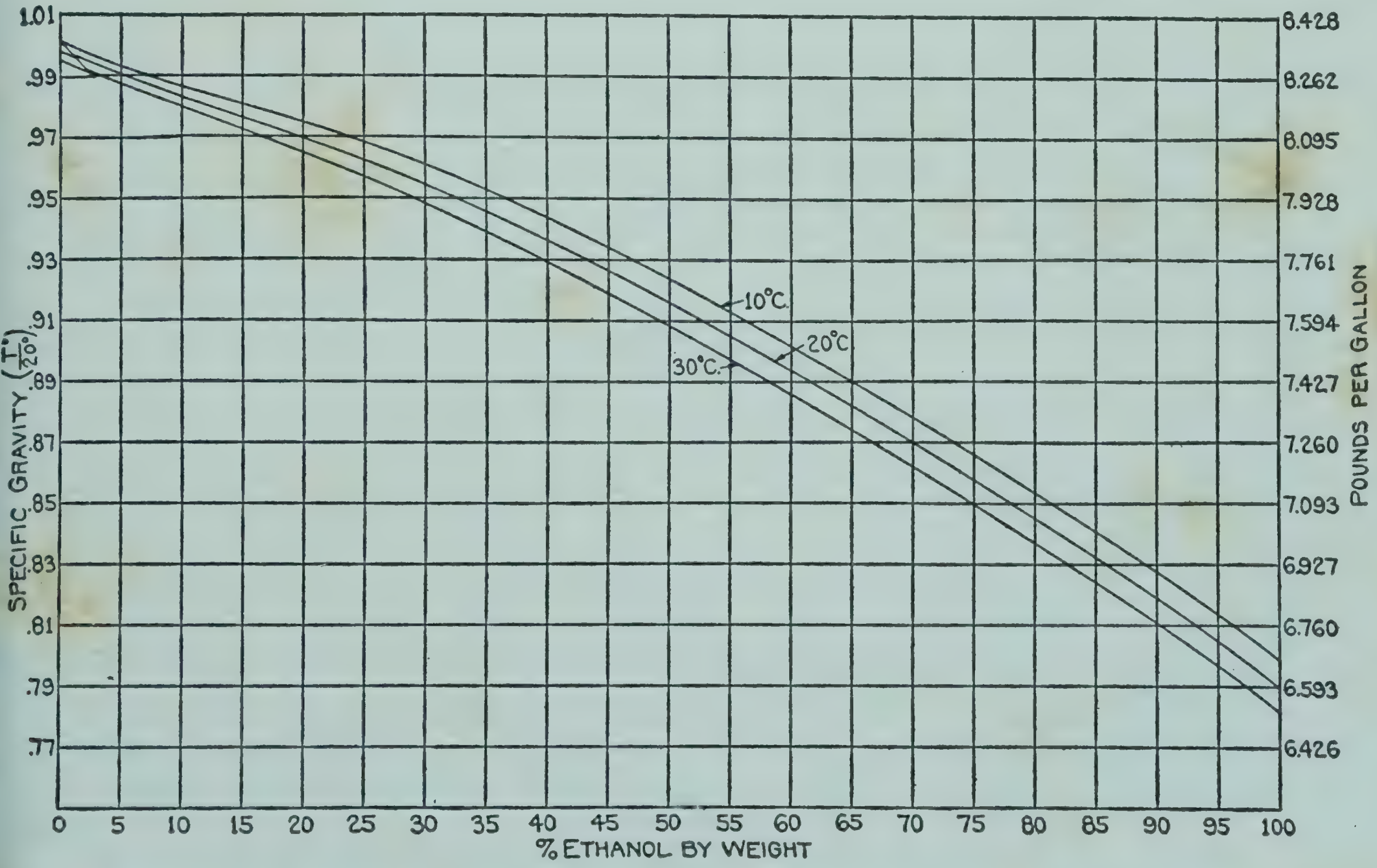

Figure 11.10. Specific Gravity and Weight per Gallon of Aqueous Solutions of Ethanol.[6]

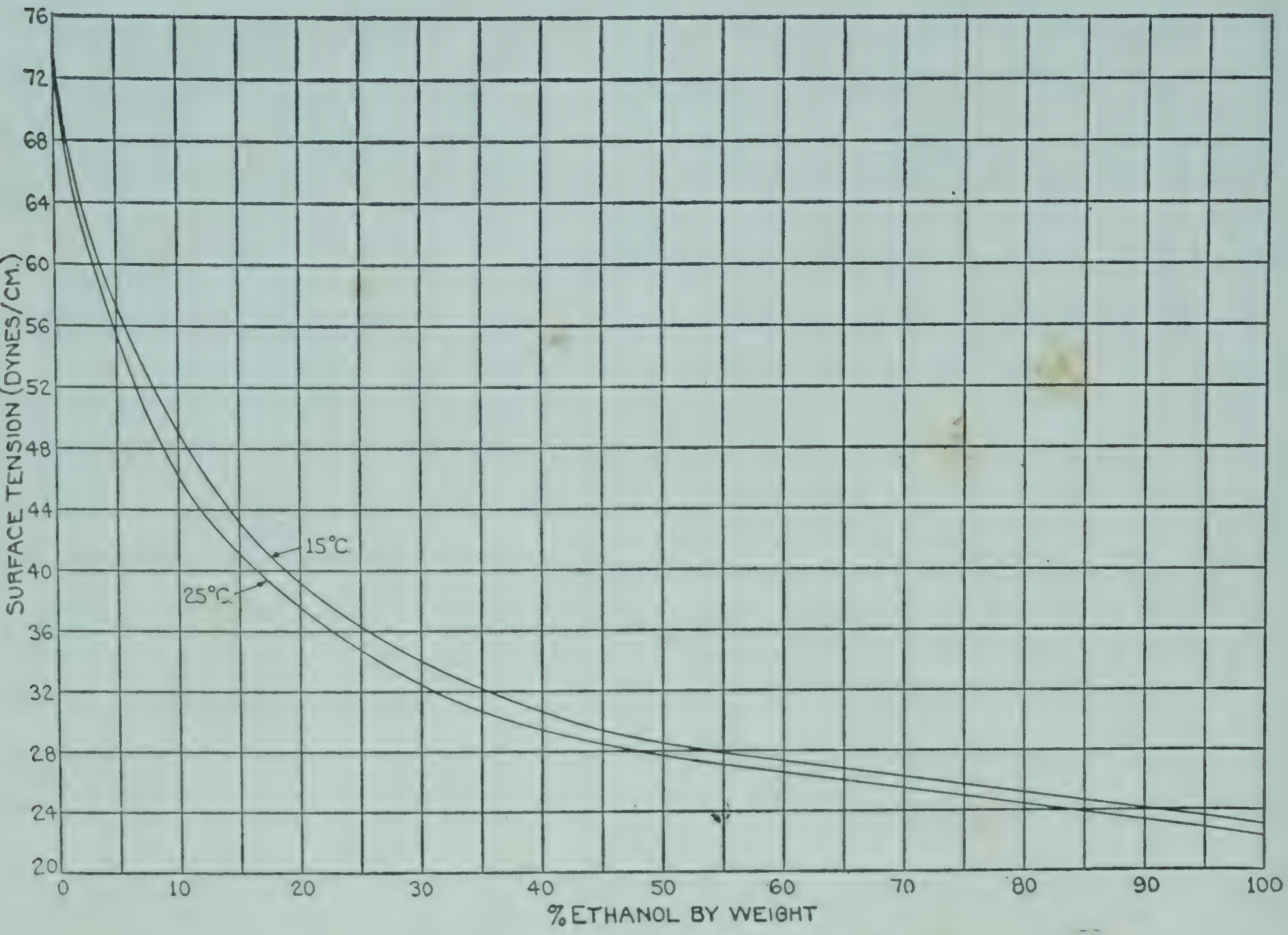

Figure 11.11. Surface Tension of Aqueous Solutions of Ethanol.[6]

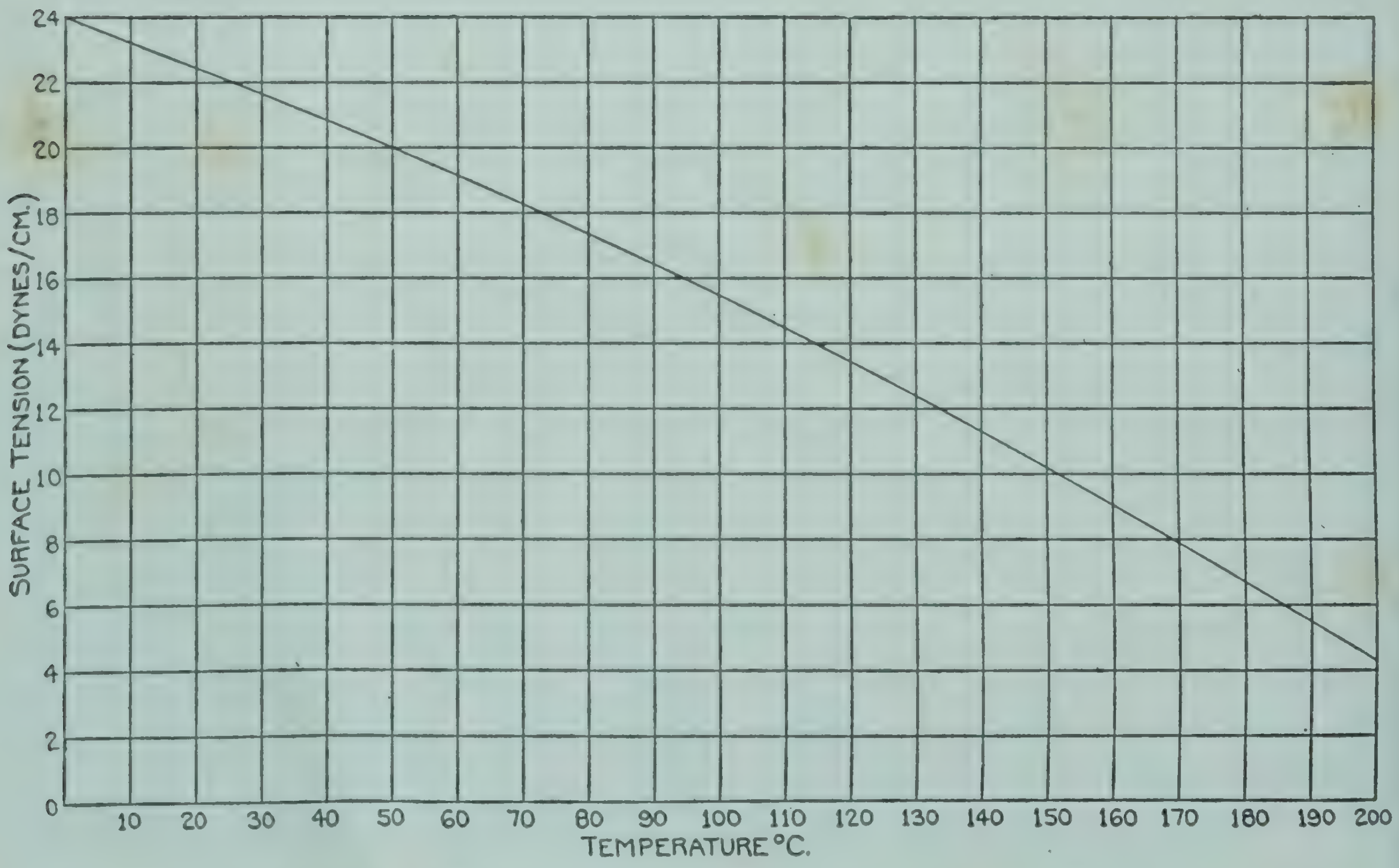

Figure 11.12. Surface Tension of Pure Ethanol at Various Temperatures.[6]

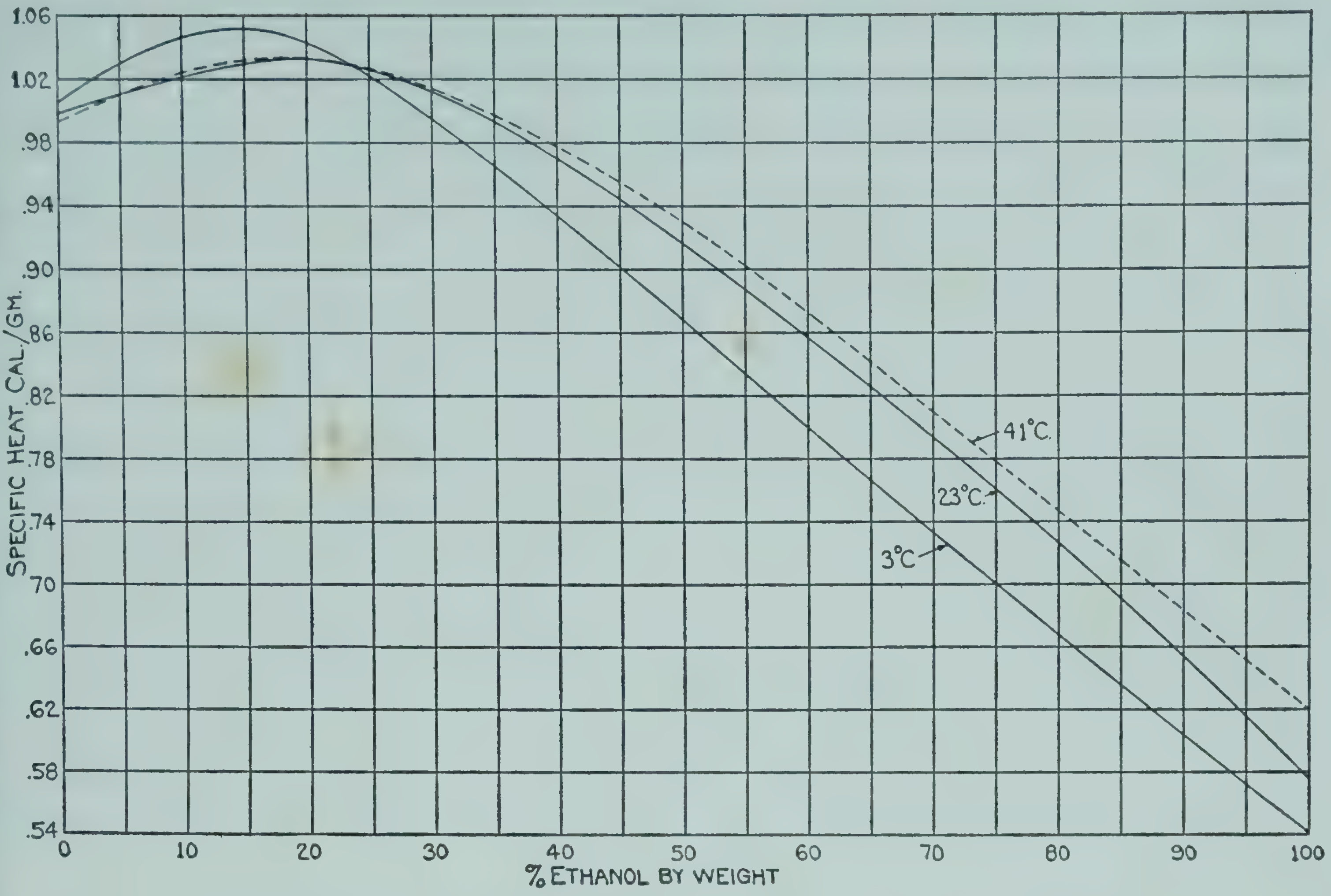

FIGURE 11.13. Specific Heat of Aqueous Solutions of Ethanol.[6]

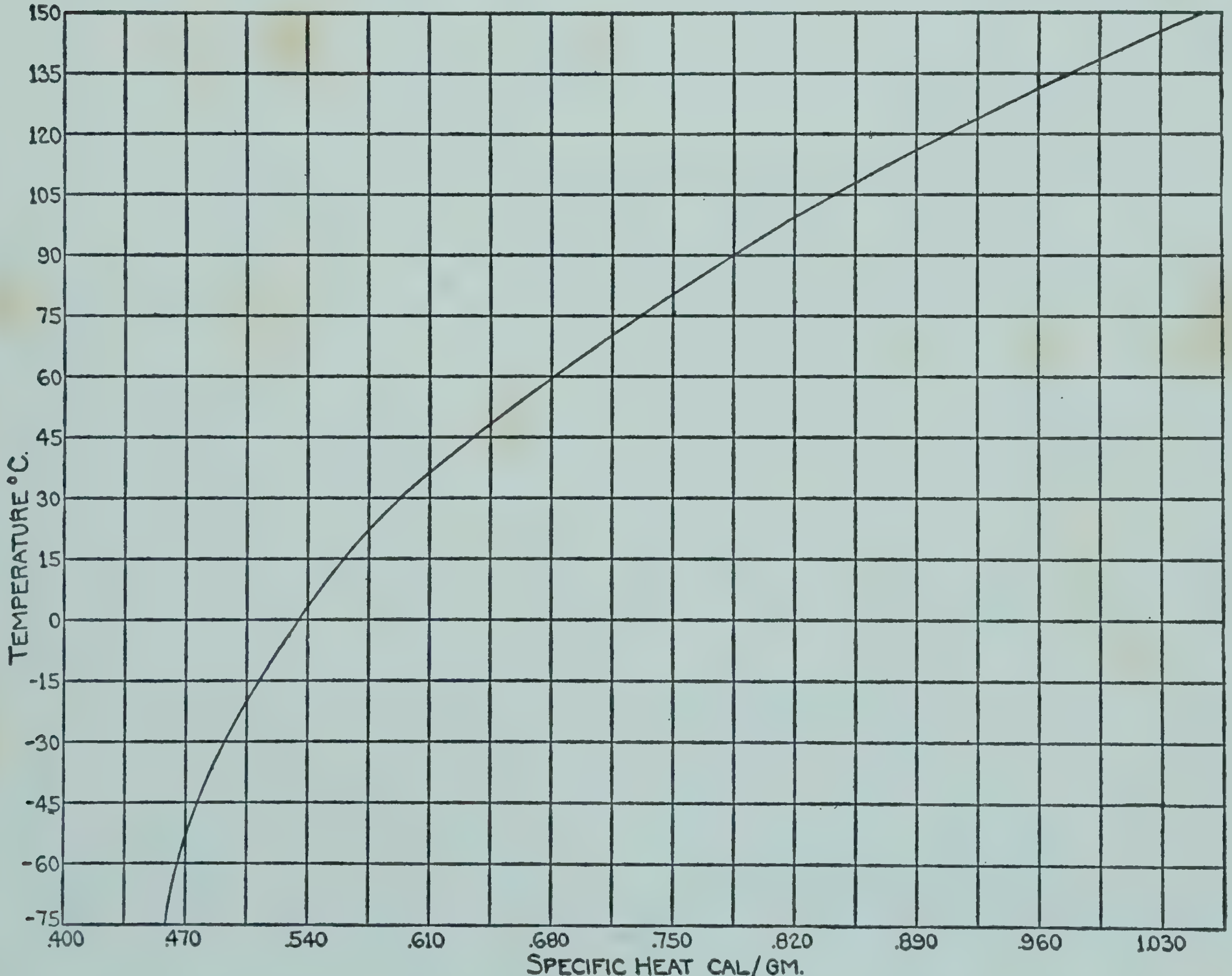

FIGURE 11.14. Specific Heat of Ethanol at Constant Pressure and Various Temperatures.[6]

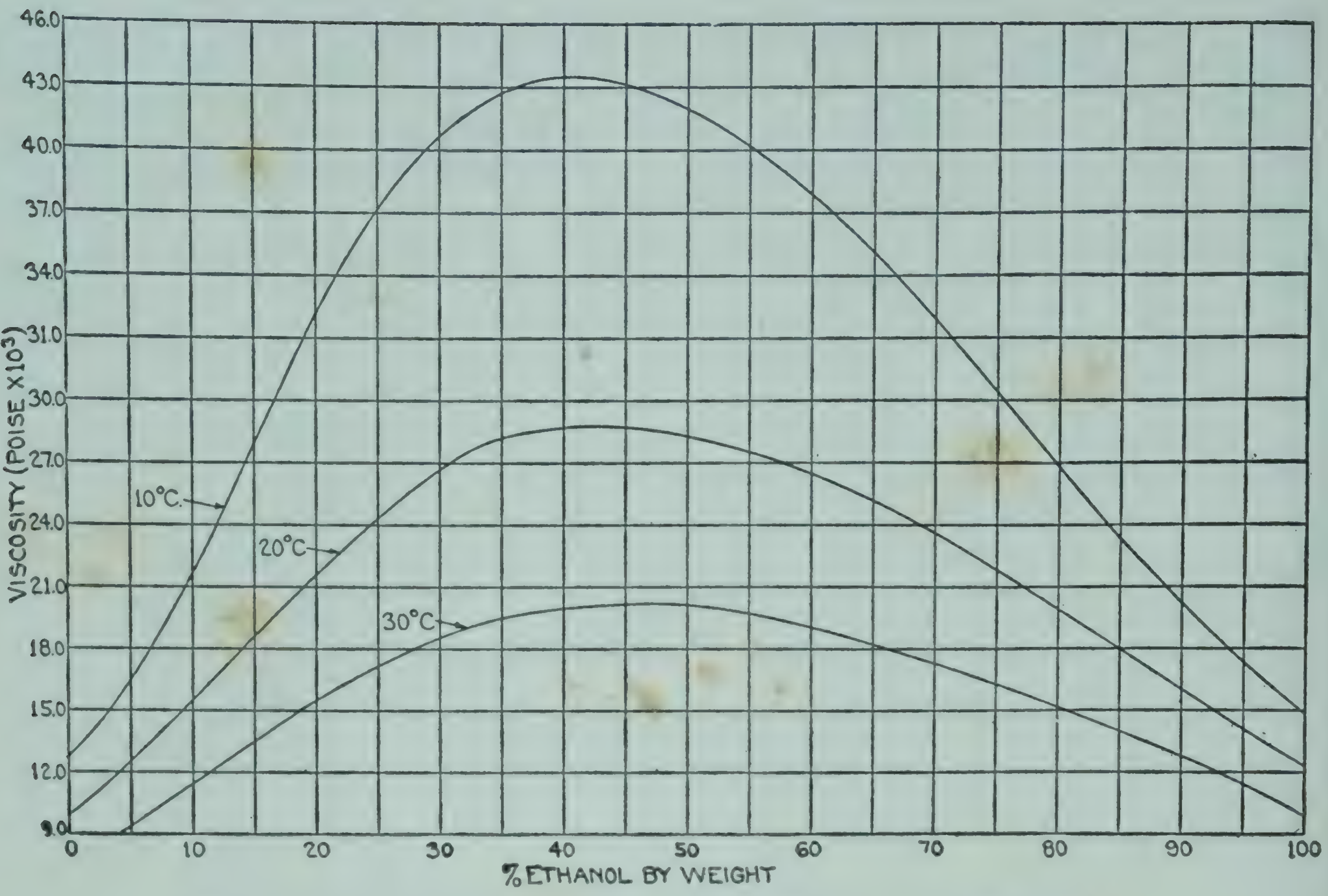

FIGURE 11.15. Viscosity of Aqueous Solutions of Ethanol.[6]

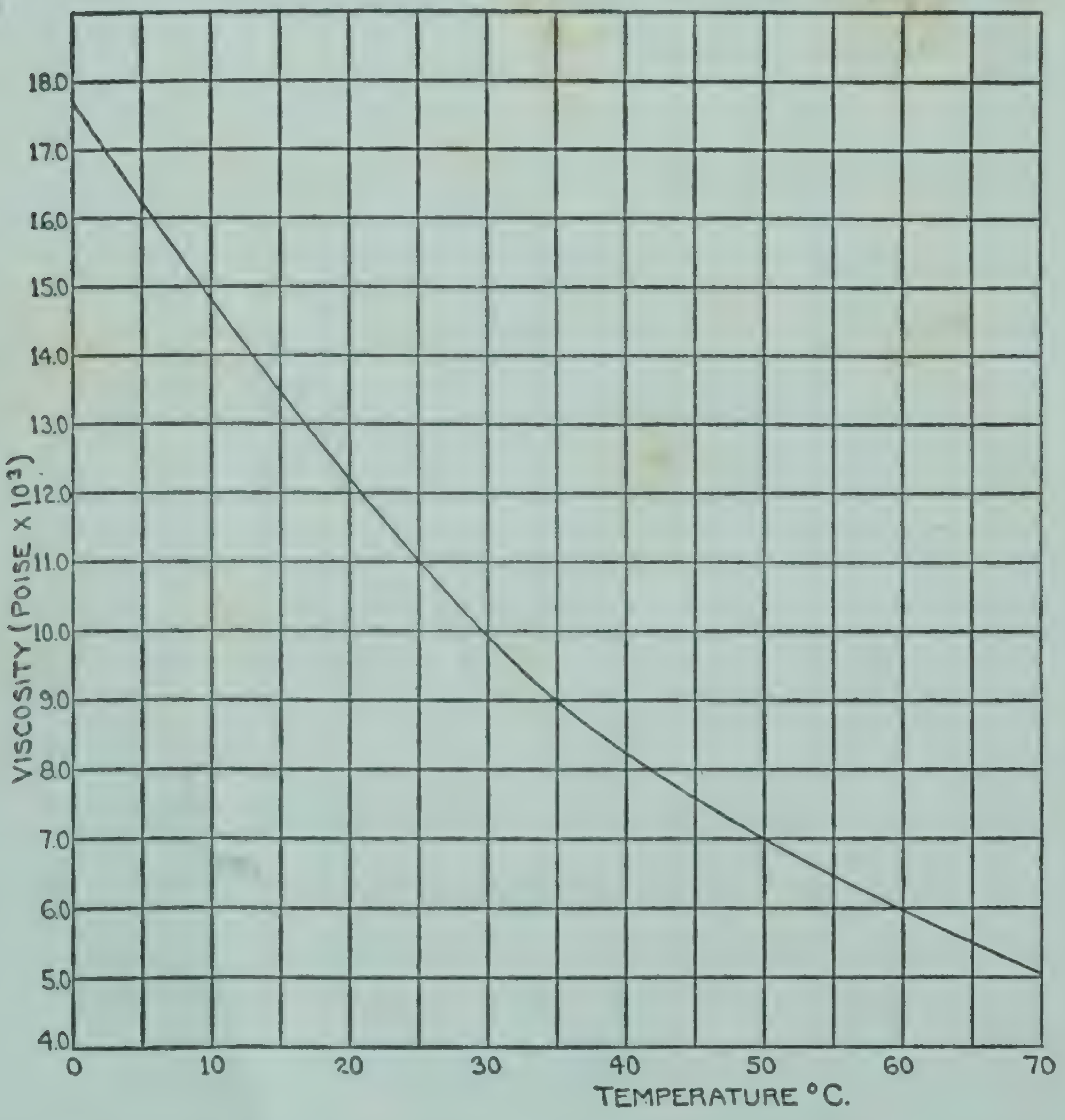

FIGURE 11.16. Viscosity of Ethanol at Various Temperatures.[6]

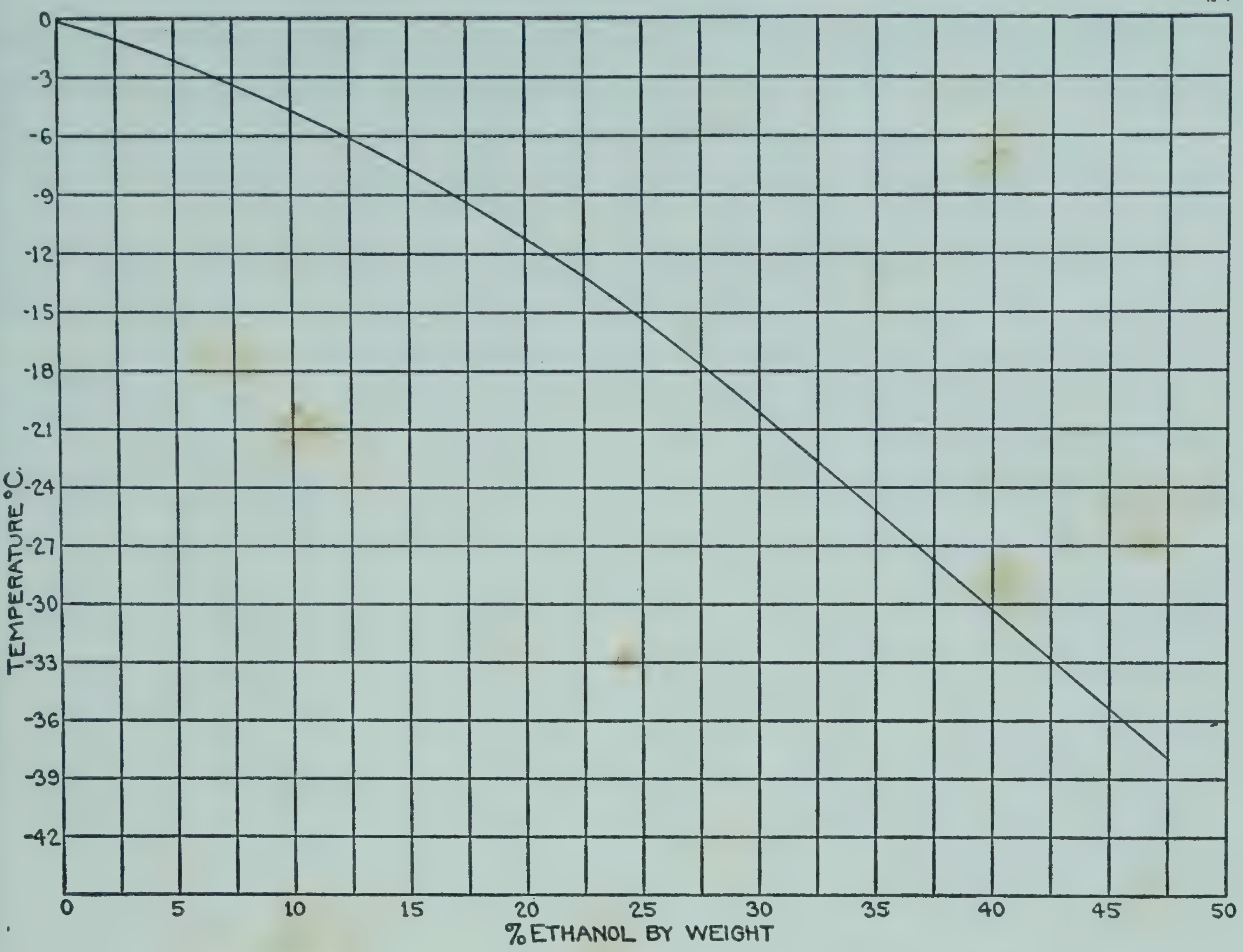

FIGURE 11.17. Freezing Point of Aqueous Solutions of Ethanol.[6]

TABLE 11.1. NUMBER OF COMMERCIALLY AVAILABLE HYDROXYL COMPOUNDS INCLUDING ALCOHOLS, GLYCOLS, AND GLYCOL-ETHERS

1925
- Isopropyl alcohol

1930
- Methyl alcohol
- Ethyl alcohol
- *n*-Propyl alcohol
- Isobutyl alcohol
- *sec*-Butyl alcohol
- Ethylene glycol
- Amyl alcohols
- Diethylene glycol
- Triethylene glycol
- Ethylene glycol monomethyl ether
- Ethylene glycol monoethyl ether
- Ethylene glycol monobutyl ether
- Diethylene glycol monoethyl ether
- Diethylene glycol monobutyl ether

1935
- *n*-Butyl alcohol
- Propylene glycol
- Ethylbutyl alcohol
- Methylamyl alcohol
- Ethylhexyl alcohol
- Diethylene glycol monomethyl ether

1940
- Dipropylene glycol
- Polyethylene glycols 200, 300, 400
- Carbowax compounds 1,500, 1,540, 4,000
- Pentaerythritol
- Polyvinyl alcohol

1945
- 2-Methyl-2,4-pentanediol
- 2-Ethyl-1,3-hexanediol
- Carbowax compounds 1,000, 6,000
- Polyethylene glycol 600
- Polypropylene glycol 150
- Allyl alcohol

Completely denatured alcohol is ethyl alcohol made unfit for beverage purposes. This is brought about by adding certain denaturants prescribed by the Bureau of Internal Revenue. Specially denatured alcohol, of which some 50 different formulas have been authorized, is also unfit for a beverage,

Table 11.2. Allocations of Ethyl Alcohol (Industrial Grade): October 1, 1944–June 30, 1945*

(Thousands of gallons 190 proof)

Use	Amount	Per cent
Total allocations	475,008	100.0
Direct military[1]	2,535	0.5
Export	40,710	8.6
Other uses	431,763	90.9
Synthetic rubber	243,246	51.2
Explosives	20,390	4.3
Plastics and synthetic resins	6,996	1.5
Chemical manufacture	84,828	17.9
Acetaldehyde	35,318	7.4
Acetic acid	12,726	2.7
Ethyl acetate	7,869	1.7
Ethers	2,616	0.6
Basic medicinal chemicals	2,238	0.5
Other ethyl esters	1,706	0.4
Other chemicals	22,325	4.6
Solvent uses	35,481	7.4
Nitrocellulose and lacquers[2]	7,719	1.6
Shellac and resins	4,731	1.0
Pharmaceuticals and cosmetics[3]	4,181	0.9
Adhesives and coatings	1,424	0.3
Inks and duplicating equipment	973	0.2
Preservatives and cleaning fluids	235	[4]
General solvents	16,218	3.4
Other uses	40,822	8.6
Antifreeze	29,652	6.3
Vinegar and foods	3,984	0.8
Miscellaneous uses and small orders[5]	7,186	1.5

[1] End-use data not available.

[2] Includes nitrocellulose dehydration.

[3] Includes toilet preparations.

[4] Less than one-tenth of one per cent.

[5] Includes alcohol assigned to "mechanical processes" not otherwise defined.

* "Facts for Industry," Bureau of the Census.

but has certain specific industrial uses. A complete list of authorized denaturants is promulgated in the Appendix to Alcohol Regulations issued by the U. S. Treasury Department (see below).

Ethyl alcohol is such a universal solvent that there remains hardly one industry in which it is not used, as can be noted from Table 11.3. The end-use pattern of industrial alcohol during World War II is shown in Table 11.2.

A marked improvement in the quality of lacquers[3] can be obtained with the use of a mixture of equal parts of butyl acetate and anhydrous ethanol. Because of its particular rate of evaporation, it imparts good flow and with the presence of butyl acetate blush formation is prevented. The following table compares the tolerance of this mixture with other solvents.

	Dilution Ratios		
Solvent	Toluene	Naphtha	50% Toluene 50% Naphtha
Ethyl acetate	3.3	1.1	1.9
Methyl ethyl ketone	4.1	0.85	1.7
Isopropyl acetate	3.0	1.1	1.9
50% Anhydrous ethyl alcohol 50% Butyl acetate	3.0	1.3	2.1

Denaturants Authorized for Completely and Specially Denatured Alcohol

Acetaldehyde
Acetone
Acetaldol
Almond oil (bitter)
Ammonia water
Animal oil
Arnica flowers, fluid extract of
Bay oil
Benzaldehyde
Benzoic acid
Benzol
Bergamot oil
Brucine
Brucine sulphate
Butyl alcohol (normal)
Camphor
Cassia oil
Cedar leaf oil
Chloroform (crude)
Chlorthymol
Cinnamon oil
Citronella oil
Cinchonidine
Cinchonidine sulphate
Cloves oil
Condensed fumes
Dehydrol–O
Diethylphthalate
Ethyl acetate
Ethylamines
Ethyl ether
Ethyl propionate
Emetine hydrochloride
Eugenol
Eucalyptol
Eucalyptus oil
Formaldehyde
Gasoline
Glycerine
Guaiacol
Iodine
Ipecac
Ipecac (fluid extract of)
Kerosene
Lavender oil
Menthol
Mercuric iodide
Methylene blue
Methyl alcohol
Methyl isobutyl ketone
Methyl propyl ketone
Methyl salicylate
Methyl violet
Mustard, volatile oil of

(continued)

Nicotine
Peppermint oil
Phenol
Phenols
Phenyl salicylate
Phenyl mercuric nitrate C. P.
Phenyl mercuric chloride C. P.
Phenyl mercuric benzoate C. P.
Pine oil
Pine needle oil
Potassium iodide
Pine tar
Pyridine bases
Quassia (fluid extract, N. F.)
Quinine
Quinine bisulphate
Quinine hydrochloride
Quinine sulphate
Resorcin
Rosemary oil
Safrol
Salicylic acid
Sassafras oil
Shellac (refined)
Sodium ethyl mercuric thiosalicylate
Sodium iodide
Sodium salicylate
Soaps
Spearmint oil
ST-115
Sucrose octa acetate
Sulphuric acid
Tertiary butyl alcohol
Thyme oil
Thymol
Turpentine oil
Vinegar
Wintergreen oil
Wood alcohol
Zinc chloride

Typical Properties

	Absolute	95%
Apparent ignition temp. in air.	371–427°C	
Boiling point	78.4°C	78.2°C
Electrical conductivity	1.35×10^{-9} recip. ohms (25°C)	
Explosive limits in air	3.7–13.7%	
Flash point (ASTM Open Cup)	18.3°C (65°F)	14°C (57°F)
Freezing point	−114.4°C	
Heat of combustion	328 kg cal./mol	
Heat of fusion	24.9 cal./g	
Heat of vaporization at B.P.	204 cal./g.	
Melting point	−116°C	
Refractive index at 15°C	1.3633	1.3651
Specific gravity at 20/20°C	0.7904	0.8089–0.8128
Specific heat at 25°C	0.581 cal./g	0.618 cal./g (23°C)
Surface tension at 20°C	22.3 dynes/cm	22.8 dynes/cm (20°C)
Viscosity at 20°C	0.0122 poise	0.0141 poise (20°C)
Vapor pressure at 20°C	43.6 mm	43.0 mm (20°C)
Weight per gallon at 20°C	6.60 lbs.	6.73 lbs. (20°C)

Typical Specifications, Chemically Pure, 96%

Acidity, free acid as acetic	0.0014 gm. per 100 cc. max.
Boiling point	78.2°C
Distillation range	100% between 77–80°C
Flash point	62°F (approx.)
Nonvolatile matter	Not more than 0.0025 g per 100 cc
Odor	Free from foreign odors when tested at high or low proof
Purity	96% ethyl alcohol by vol,. min.
Reducing substances	Not less than 45 min. permanganate time
Specific gravity at 15.6/15.6°C	0.8121
Solubility in water	In all proportions and without turbidity

TABLE 11.3. SPECIALLY DENATURED ALCOHOL:† STATISTICS ON USES IN THE UNITED STATES, FISCAL YEAR ENDED JUNE 30, 1949*

PRODUCT OR USE	AMOUNT USED		AMOUNT RECOVERED FOR REUSE
	New	Reused‡	
	Wine gallons		
Cellulose resin, and related products:			
Lacquers, varnishes, and enamels:			
Cellulose	534,810	308,731	355,666
Synthetic resins (with or without natural resins but containing no cellulose compounds)	410,894	4,242	101
Shellac (containing no cellulose or synthetic resins)	2,294,819	—	—
Other natural resins (containing no cellulose, synthetic resin or shellac	174,632	—	—
Candy glazes	100,056	—	—
Other coatings	12,451	30,693	—
Total	3,527,662	343,666	355,767
Plastics:			
Cellulose compounds	334,759	202,421	168,020
All other plastics (containing no cellulose)	2,861,915	1,094,164	1,086,881
Total	3,196,674	1,296,585	1,254,901
Photographic film (including emulsions)	206,288	690,743	206,000
Transparent sheeting	147,574	919,261	1,016,672
Cellulose intermediates	34,240	—	—
Explosives	107,866	688,062	621,433
Polishes	24,421	—	—
Adhesives	50,450	—	—
Soldering flux	58,346	—	—
Inks, stains, and dye solutions (containing no cellulose or resins)	101,519	—	—
Total cellulose, resin and related products	7,455,040	3,938,317	3,454,773
Solvents and thinners for cellulose, shellac, resin products, etc.:			
Proprietary solvents	18,648,380	—	—

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* U. S. Treasury Department, Bureau of Internal Revenue, Alcohol Tax Unit.

† Includes specially denatured rum.

‡ Represents amounts reused after recovery from processes where the alcohol has not become a part of the finished product. Such alcohol may have been recovered during the fiscal year 1940 or prior thereto and from any of the listed processes.

TABLE 11.3—*Continued*

PRODUCT OR USE	AMOUNT USED		AMOUNT RECOVERED FOR REUSE
	New	Reused‡	
	Wine gallons		
Other industrial thinners	297,618	9,925	—
Total	18,945,998	9,925	—
Toilet preparations:			
Hair and scalp preparations	1,057,538	115	—
Shampoos	448,476	—	—
Bay rum	139,695	—	—
Face and hand lotions	1,212,174	—	—
Body deodorants	162,170	—	—
Toilet waters	1,566,913	—	—
Perfume and perfume tinctures	100,574	—	—
Toilet soaps (including shaving cream)	24,841	—	—
Mouth washes	836,417	—	—
Tooth cleaning preparations	24,413	—	—
Total	5,573,211	115	—
Processing industrial, food, drug, and other products:			
Nitrocellulose (dehydration of)	4,020,822	18,123,845	18,789,041
Sodium hydrosulfite	318,383	12,670,330	12,592,920
Wood rosin and synthetic resins	1,141,655	23,019,391	23,011,544
Petroleum oils	631,713	7,150,011	7,188,806
Food products other than pectin	14,464	16,957	13,687
Drug products:	171,943	809,444	803,911
Drug extracts			
Glandular products and vitamins	1,185,526	9,590,108	9,681,334
Medicinal chemicals	699,617	2,626,044	2,650,129
Miscellaneous (including pill and tablet manufacture)	85,137	177,000	170,579
Dyes and intermediates	659,379	360,262	550,449
Perfume materials and fixatives	37,842	73,461	73,020
Photographic developers	65,411	50	—
Other chemicals	758,541	2,048,202	2,532,595
Miscellaneous	144,725	1,695,080	1,605,405
Total	9,935,158	78,360,185	79,663,420
Pharmaceutical products for external use:			
Rubbing alcohol	2,427,216	—	—
U. S. P. and N. F. preparations:			
Witch hazel	112,616	—	—
Liniments	84,392	—	—
Collodions	25,112	—	—

TABLE 11.3—*Continued*

PRODUCT OR USE	AMOUNT USED		AMOUNT RECOVERED FOR REUSE
	New	Reused‡	
	Wine gallons		
Antiseptics	3,765	—	—
Miscellaneous	23,685	—	—
Total	249,570	—	—
Tinctures of iodine (official and non-official)	35,645	—	—
Other preparations not U.S.P. or N.F.	402,994	12	32
Total pharmaceutical products for external use	3,115,425	12	32
Cleaning, preserving, and flavoring preparations:			
Tobacco sprays and flavors	727,674	—	—
Cleaning preparations (including cleaning operations)	138,819	2,967	13,142
Deodorant sprays (nonbody)	61,098	92	91
Disinfectants, insecticides, etc.	56,592	1,876	—
Sterilizing and preserving solutions	35,252	—	—
Embalming fluids and related products	16,458	—	—
Industrial soaps	102,139	516	516
Photoengraving and rotogravure use	82,764	—	—
Miscellaneous	199,246	237	—
Total	1,420,042	5,688	13,749
Converted as a raw material in chemical manufacturing:			
Vinegar	3,970,594	—	—
Acetic acid	3,254,210	—	—
Ethyl acetate	5,326,388	880,378	602,243
Ethyl chloride	10,173,571	55,670	118,952
Other ethyl esters	2,737,161	1,143,799	1,531,337
Dyes and intermediates	95,916	239,557	31,545
Aldehydes	68,253,434	17,889,355	17,878,655
Ether, ethyl	1,033,202	19,498	—
Ethers, glycol and other	1,909,170	12,550,202	12,552,002
Drugs and medicinal chemicals	19,897	152,933	153,023
Xanthates	414,179	—	—
Fulminate of mercury	23,049	—	—
Ethylene gas	47,693	—	—
Synthetic rubber	1,427,787	—	—
Rubber accelerators	609,825	—	—
Miscellaneous	2,403,031	1,878,046	1,864,102
Total	101,699,107	34,809,438	34,731,859

Table 11.3—*Continued*

PRODUCT OR USE	AMOUNT USED		AMOUNT RECOVERED FOR REUSE
	New	Reused‡	
	Wine gallons		
Fluid uses:			
Anti-freeze	54	—	—
Brake fluids	180	—	—
Cutting oils	20,659	4,194	—
Other fluid uses (including door checks)	73,946	8,751	4,767
Total	94,839	12,945	4,767
Fuel uses:			
Motor fuels	750	—	—
Airplane fuel	150,511	—	—
Other fuel uses	190,754	—	—
Total	342,015	—	—
Laboratory and experimental uses	418,664	22,414	20,379
Grand total	148,999,499	117,159,039	117,888,979

Table 11.3a. Consumption of Ethyl Alcohol (Industrial Grade): January 1, 1943–June 30, 1945*
(Thousands of gallons 190 proof)

USE	TOTAL		JAN. 1–JUNE 30, 1945	JAN. 1–DEC. 31, 1944	JAN 1–DEC. 31, 1943
	Amount	Per cent			
Total consumption	1,317,500	100.0	283,200	605,800	428,500
Direct military[1]	82,200	6.2	15,100	27,200	39,900
Lend-lease	142,900	10.9	23,000	56,900	63,000
Synthetic rubber	611,200	46.4	154,700	329,600	126,900
Antifreeze	92,100	7.0	9,500	31,800	50,800
Indirect military and civilian	389,100	29.5	80,900	160,300	147,900

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[1] This item differs from "direct military" in Table 11.2 in that it includes all material identified by military order numbers some of which is distributed among ultimate end-uses in Table 11.2.

* "Facts for Industry," Bureau of the Census.

***n*-Propyl Alcohol.** *n*-Propyl alcohol ($CH_3CH_2CH_2OH$, propanol) is a colorless flammable volatile liquid. It is recovered as a by-product of high pressure methanol synthesis and in the propane-butane oxidation process. Generally, it has about the same solvent properties as ethyl alcohol with the added feature of having a higher boiling point. It is a solvent for vegetable oils for natural resins like soft copals, rosin, shellac and a number of synthetic resins. It is similar to ethyl alcohol in its solvency for cellulose ethers and esters.

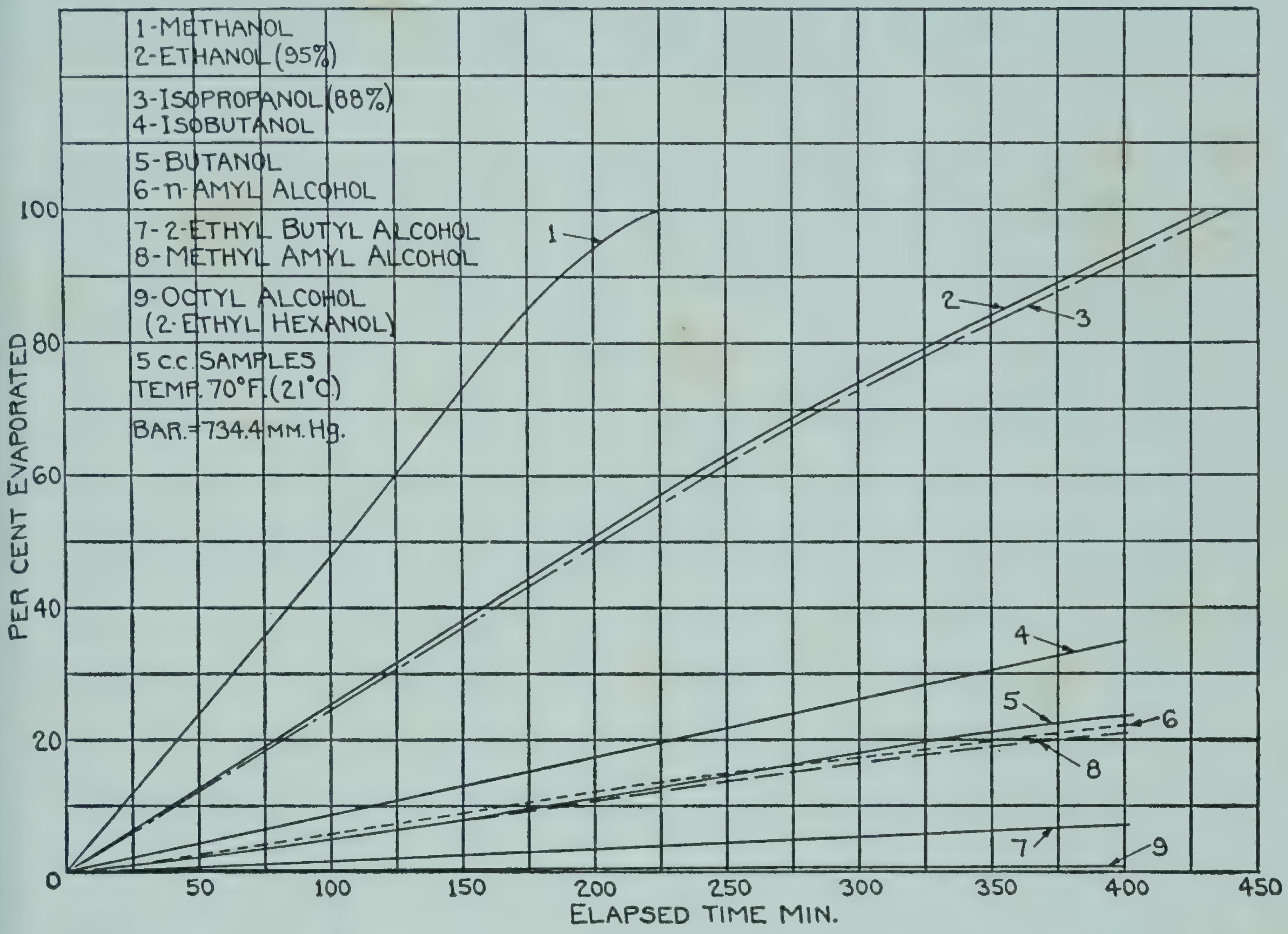

FIGURE 11.18. Evaporation Rate of Alcohols at Room Temperature.[6]

Isopropanol. (Isopropyl alcohol, secondary propyl alcohol, per-spirit, petrohol, avantine) ($CH_3 \cdot CHOH \cdot CH_3$). Isopropanol was first prepared in 1855 by Berthelot while he was engaged in the process of regenerating *n*-propyl alcohol. He dehydrated *n*-propyl alcohol, obtaining propylene; then by hydrating this olefin, he obtained isopropyl alcohol without recognizing it as being distinct from *n*-propyl alcohol. Seven years later Friedel also stumbled upon it, and he too failed to recognize its identity. His method of making it was by reducing acetone with sodium amalgam. Its true nature was finally realized by Kolbe, who named it isopropyl alcohol. Today practically all isopropanol is made synthetically from propylene which is obtained by cracking petroleum hydrocarbons. A small percentage of the domestic output is produced by the reaction of natural gas hydrocarbons.

The commercial product is an azeotropic mixture containing 91.09 per cent by volume isopropanol and 8.91 per cent by volume water (87.7% by wt. and 12.3% by wt.). Like ethanol, isopropanol can be made anhydrous by methods involving azeotropic distillation. Isopropanol is a colorless liquid with a pleasant characteristic odor. It is miscible with water in all proportions, but it can be salted out by saturating the aqueous solution with sodium chloride or other salts. It will dissolve essential and other oils, alkaloids, gums, shellac, sandarac, rosin, mastic, copals, some synthetic resins, waxes, hydrocarbons, esters, and many organic and inorganic compounds. Because of its high latent solvent properties for cellulose derivatives it is used in lacquers and thinner mixtures.

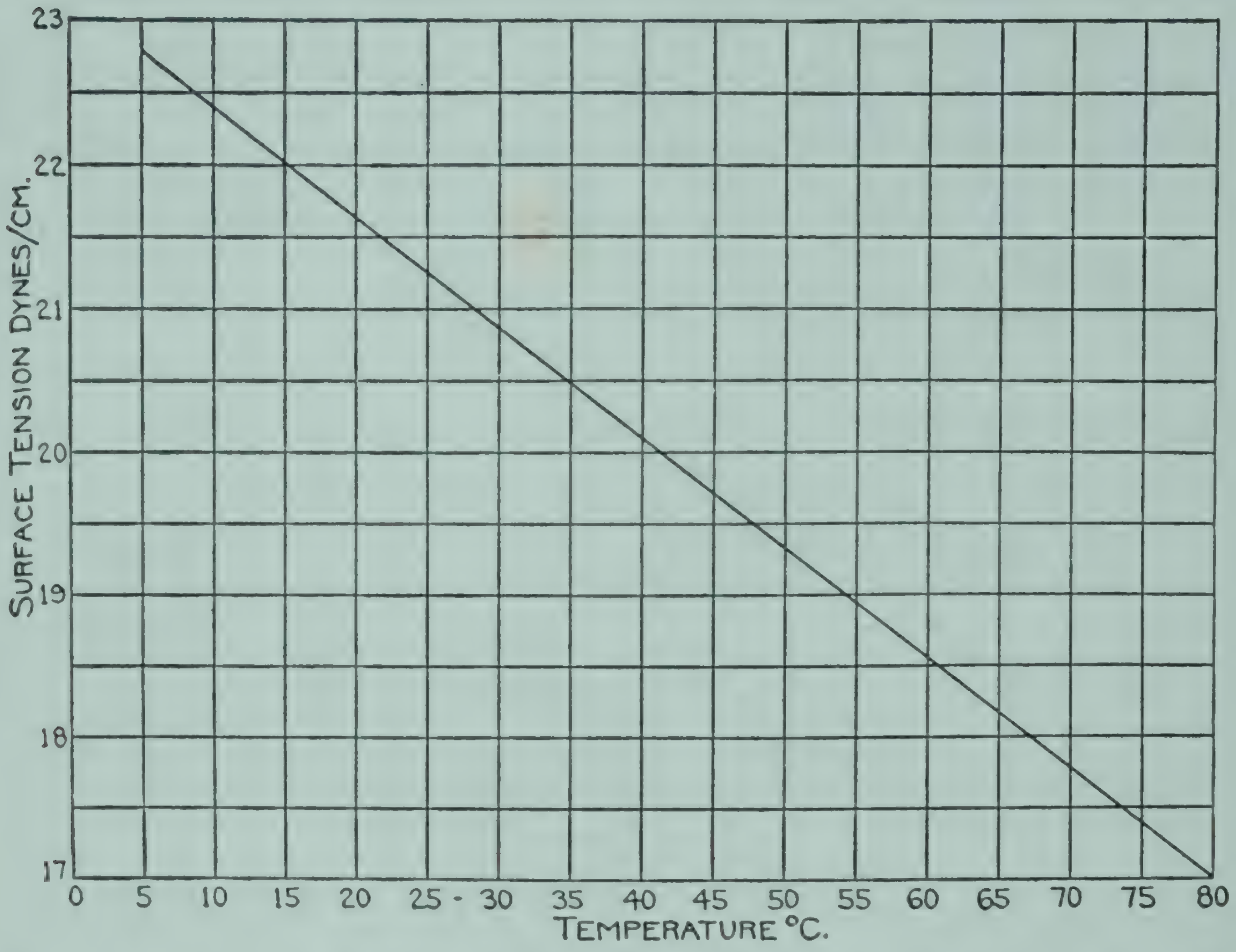

Figure 11.19. Surface Tension of Isopropanol at Various Temperatures.[6]

In chemical properties, isopropanol resembles n-propyl alcohol. Having germicidal and disinfectant properties it can be substituted for ethanol in liniments, skin lotions, cosmetics, creams, pharmaceuticals and hair tonics It is not approved for use in preparations to be taken internally.

It is used as a solvent in perfumes, in extraction processes, as a preservative, in nitrocellulose lacquer formulations and in many dye solutions such as hair, inks, leather, and shoes. The following is a list of dyes in ethyl and isopropyl alcohols showing their degree of solubility.

Dye	Solubility in Alcohol	
	Ethyl 99%	Isopropyl 99%
Auramine O Conc	4.8% Wt.	1.3% Wt.
Bismark Brown	3.81	0.297
Chrysoidine R	5.23	0.97
Chrysoidine Y	2.50	0.58
Fuchsine	4.65	0.966
Malachite Green	13.80	2.14
Metanile Yellow	0.69	0.095
Methyl Violet Crystals	Soluble	Soluble
Methylene Blue	0.099	0.097
Nigrosine SSBS	2.30	2.25
Rodamine B Extra	12.50	3.20
Rodamine 6GDNX	14.40	2.38
Safranine	2.84	0.88

Isopropanol is an ingredient of liquid soaps, and of window cleaner preparations. In the cosmetic field it is employed in preparations for the removal of facial make-up and in preparations for permanent waving where its solvent action for gum karaya is utilized. The following indicates the degree of solubility in isopropanol of natural gums.[4]

Gum	Solubility in isopropanol	
	91%	99%
Congo Ivory	P	P
Hard Dark Amber	P	P
Medium Pale	N	N
Damar Std. Batavia	I	I
Batavia E. Seeds	P	P
East India Batu Bold Scraped	L	L
Bold Black Scraped	L	L
Pale Bold Singapore	L	L
Kauri, No. 1 Brown	N	N
Manila, Bold Medium Dark	N	N
CME	N	N
DBB Soluble Copal Chips	N	N
Loba C	N	N
MA	N	N
Pontianak Genuine Bold	S	S
Genuine Nubs	S	S
Genuine Small Chips	N	N

S—Soluble-but Cloudy
N—Nearly all soluble
P—Partially soluble
L—Slightly soluble
I—Insoluble

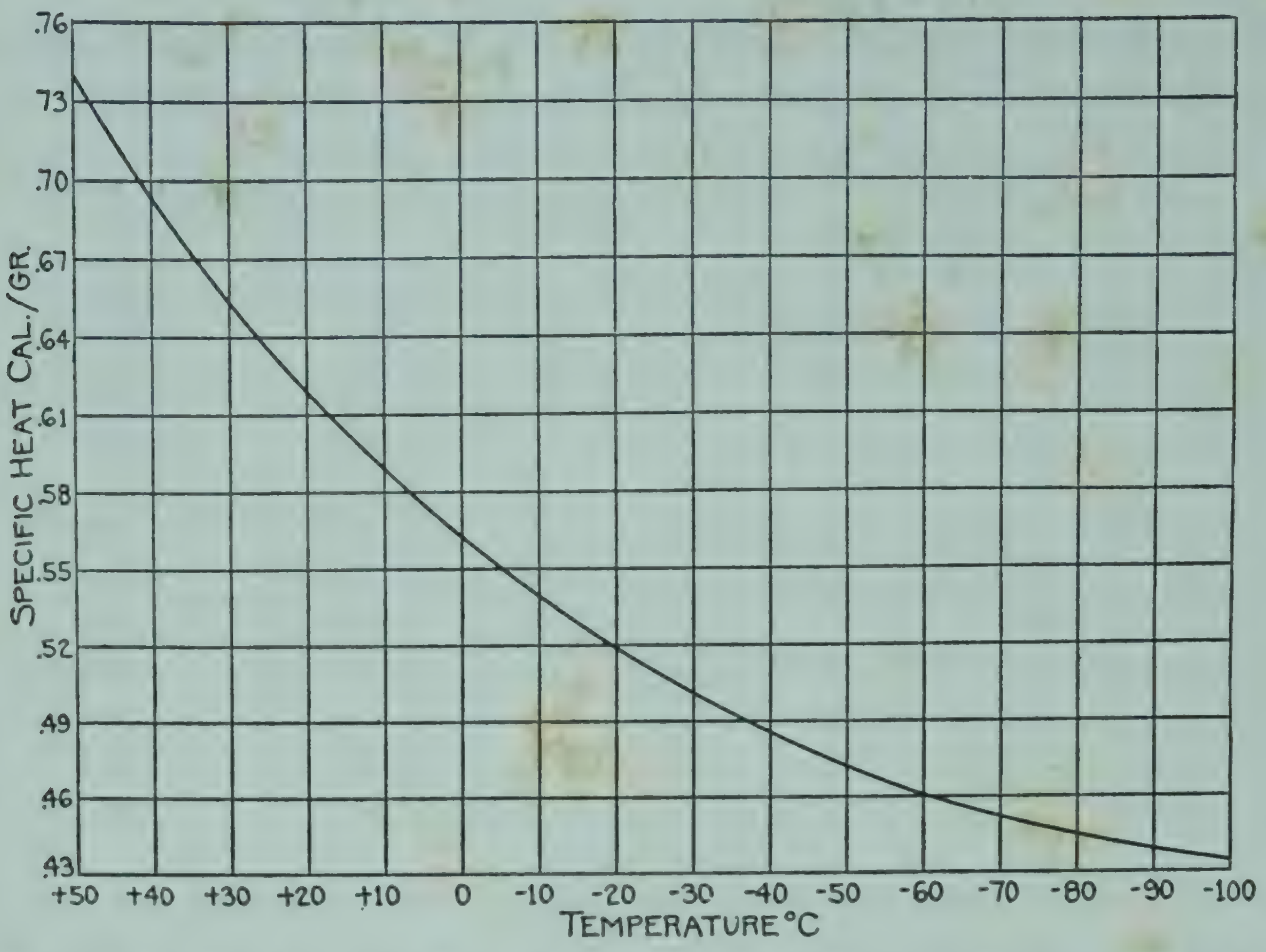

FIGURE 11.20. Specific Heat of Isopropanol at Various Temperatures.[6]

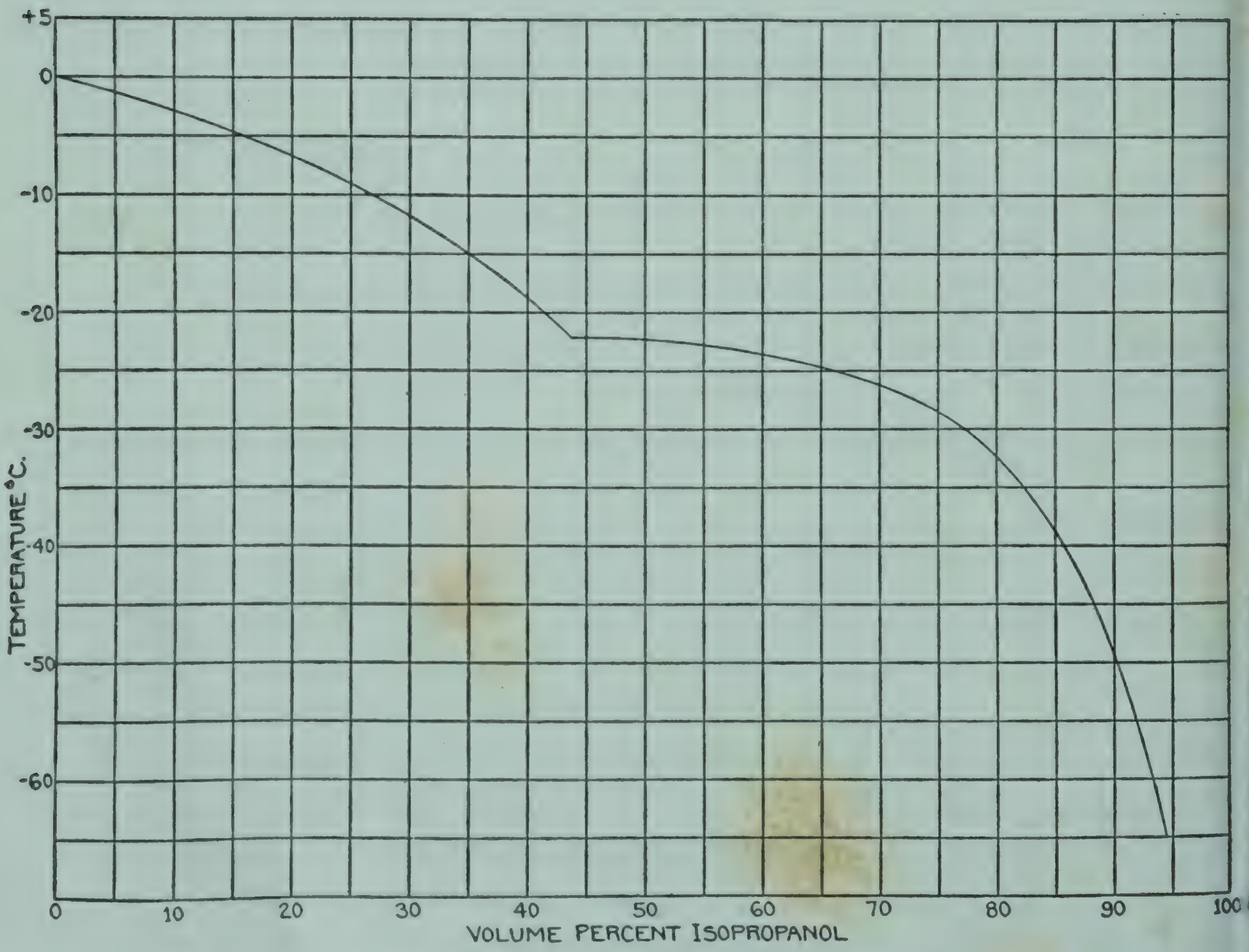

FIGURE 11.21. Freezing Point of Isopropanol-Water Mixtures (Temperature of Initial Crystallization).[32]

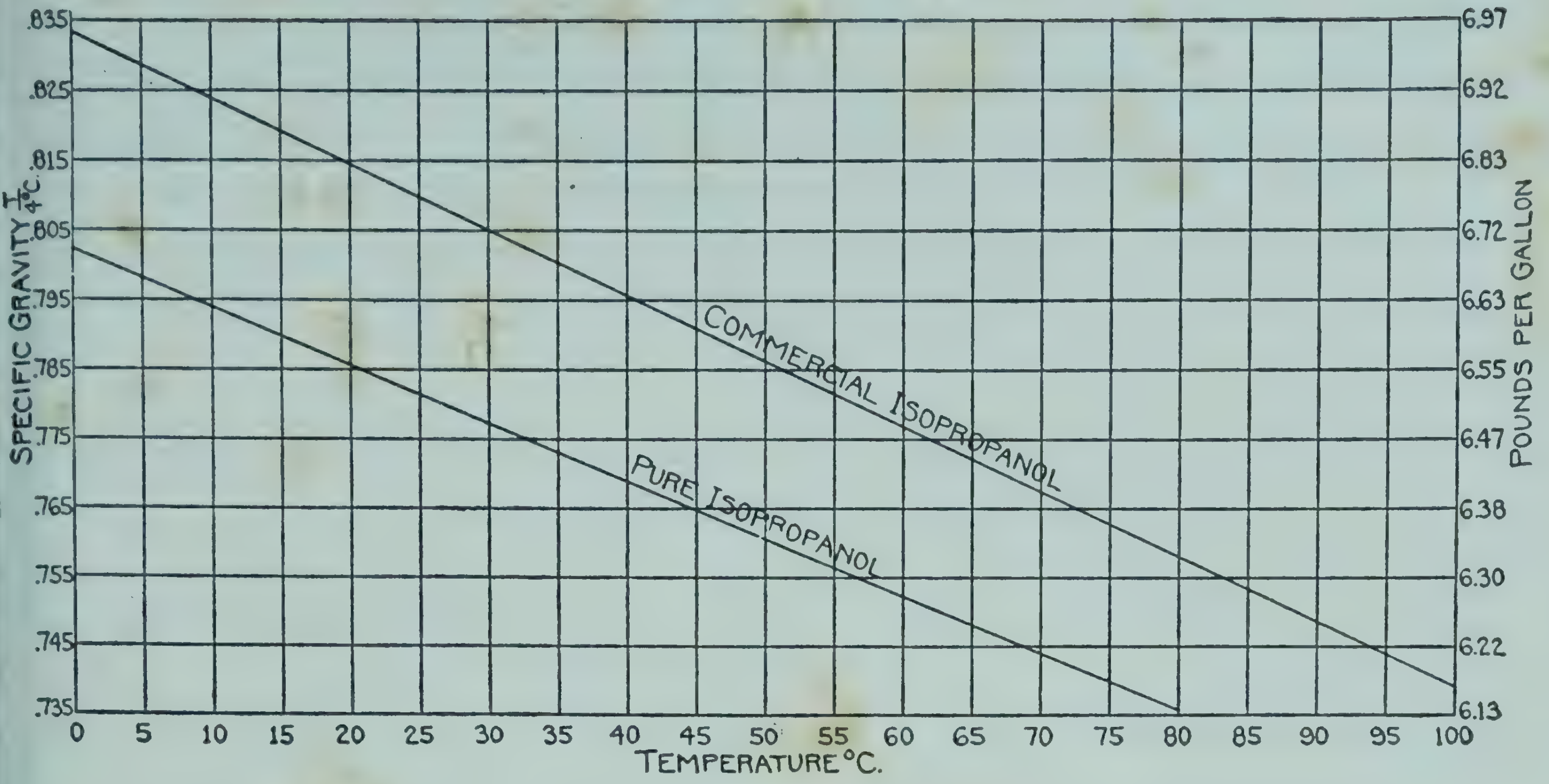

FIGURE 11.22. Specific Gravity and Weight per Gallon of Isopropanol at Various Temperatures.

When mixed with gasoline isopropanol shows a water tolerance which is superior to other alcohol mixtures. The following presents a comparison of gasoline mixtures of ethyl and isopropyl alcohols.

Alcohol in Gasoline	Cc of Water Per Imperial Gallon	
	Ethyl	Isopropyl
1% Vol	10.0	12.5
10% "	16.9	19.7
15% "	28.6	38.5
20% "	40.4	64.0
25% "	51.5	100.0

Isopropanol exhibits greater solvent power for petroleum wax than for petroleum oil.

Temperature (°C)	Grams Dissolved/100 Grams of Isopropanol[4]	
	Wax	*Oil*
10	0.05	7.5
15	1.5	8.5
20	2.5	10.5
25	2.8	13.0
28	3.5	14.0

Because it dissolves both oils and water isopropanol is used as a coupling and stabilizing agent in oil emulsion and will increase oil penetration. It is also used in the manufacture of white oils, for the extraction of sulfonic acids from the petroleum oils.

Other uses for isopropanol (Table 11.4) include its combination with methanol as an antifreeze and in hydraulic brake fluids. Mixed with glycerin, it is an ingredient of deicing fluids for airplane fuselages, and also for degreasing and drying metals in preparation for electroplating. Burlage has outlined the advantages of isopropanol as a solvent in pharmaceutical manufacturing; Table 11.5 shows the solubility of 27 local anesthetics in this solvent.

TABLE 11.4. ALLOCATIONS OF ISOPROPYL ALCOHOL: JANUARY 1, 1944–JUNE 30, 1945*
(Thousands of gallons of mixed grades)

USE	TOTAL		JAN. 1–JUNE 30, 1945	JULY 1–DEC. 31, 1944	JAN. 1–JUNE 30, 1944
	Amount	Per cent			
Total allocations	123,706	100.0	44,506	41,785	37,415
Foreign	159	0.1	36	85	38
Other uses	123,547	99.9	44,470	41,700	37,377
Chemical uses	92,258	74.6	32,053	30,972	29,233
Acetone	86,291	69.8	29,899	29,037	27,355
Isopropyl acetate	4,028	3.3	1,568	1,346	1,114
Xanthates	139	0.1	39	48	52
Other chemical uses[1]	1,800	1.4	547	541	712
Technical uses	31,289	25.3	12,417	10,728	8,144
De-icing and antifreeze	11,152	9.0	3,574	4,898	2,680
Technical coatings	4,832	3.9	1,764	1,466	1,602
Rubbing alcohol	2,941	2.4	1,728	550	663
Solvents, cleaners, blends	2,156	1.7	935	642	579
Plastics and resins	1,956	1.6	737	598	621
Drugs and cosmetics	1,737	1.4	863	436	438
Textile processing	986	0.8	348	408	230
Pectin and zein	898	0.7	361	283	254
Gasoline antioxidants	604	0.5	192	214	198
Disinfectants and germicides	477	0.4	162	108	207
Brake fluids	475	0.4	220	108	147
Miscellaneous uses and small orders[2]	3,075	2.5	1,533	1,017	525

[1] Includes chemicals for laboratory use.

[2] Includes embalming fluids.

* "Facts for Industry," Bureau of the Census.

Blending of Alcoholic Solutions. "Since a contraction takes place when alcohol and water are mixed, blending of alcoholic solutions should be conducted on a weight basis. If great accuracy is not required this con-

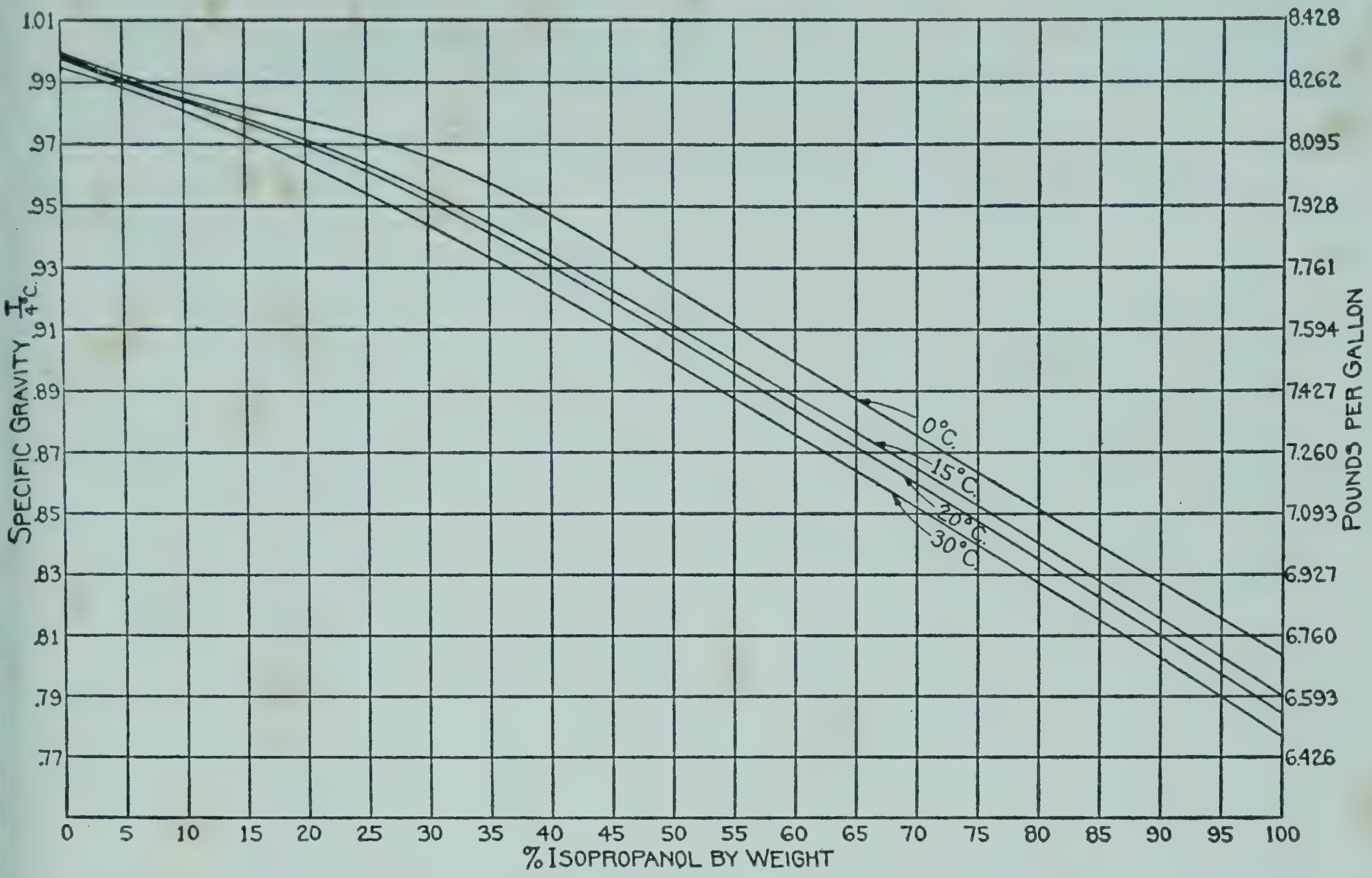

FIGURE 11.23. Specific Gravity and Weight per Gallon of Water-Isopropanol Mixtures.

traction may be disregarded, then volumes and volume percentages may be used in place of weight and weight percentages in the following formulas. The error caused by this practice becomes quite small when diluting solutions containing 70 per cent or less isopropanol or when mixing solutions already diluted.

A. To mix alcohol and water:

$$W_1 = \frac{(W \times P)}{P_1} - W$$

W = weight of solution on hand
W_1 = weight of water to be added
P = weight per cent alcohol in solution
P_1 = weight per cent alcohol in desired solution.

B. To mix two alcoholic solutions:

$$P = \frac{(W_1 \times P_1) + (W_2 \times P_2)}{(W_1 + W_2)}$$

or

$$W_2 = \frac{W_1(P_1 - P)}{(P - P_2)}$$

W_1 = weight of first solution
W_2 = weight of second solution
P_1 = weight per cent of alcohol in first solution
P_2 = weight per cent of alcohol in second solution
P = weight per cent of alcohol desired in the mixture."

TABLE 11.5. SOLUBILITIES OF LOCAL ANESTHETICS IN ISOPROPYL ALCOHOL*

NAME OF COMPOUND	SOLUBILITY, GM./100 CC. OF SOLUTION
Alypin Base (Amydricaine)	Liquid–miscible in all proportions
Alypin Hydrochloride N. N. R. (Amydricaine Hydrochloride)	38.0844
Amylsine Hydrochloride N. N. R. (Amyclaine)	0.7768
Aminocaine (Amylcaine)	49.5370
Apothesine Hydrochloride N. N. R.	5.7710
Borocaine (Ethocaine Borate)	2.3290
Butyl Aminobenzoate U. S. P. (Butesin)	47.0840
Butesin Picrate N. N. R.	9.2500
Diothane Base	38.7700
Diothane Hydrochloride N. N. R.	0.5710
Ethacaine	36.2570
Ethyl Aminobenzoate U. S. P. (Benzocaine)	16.8430
(Benzocaine)	16.6450
Eucupin Base	34.3030
Eucupin Dihydrochloride	7.8640
Intracaine	1.6070
Metycaine Base	Liquid–miscible in all proportions
Metycaine Hydrochloride N. N. R.	2.9140
Nupercaine Hydrochloride N. N. R. (Dibucaine)	Insufficient sample greater than 1 Gm. in 2; 4 cc.
Orthoform N. N. R. (Orthoform-New)	12.0450
Panthesine	1.5160
Phenacaine Base (Holocaine Base)	4.9960
Procaine Base	41.8780
Procaine Butyrate	69.4800 (unstable)
Procaine Hydrochloride U. S. P.	0.6030
Tetracaine Base (Pontocaine Base)	36.6400
Tetracaine Hydrochloride U. S. P. (Pontocaine Hydrochloride)	1.5350
Tutocaine Hydrochloride (Butamin)	0.1980

* Burlage, H. M., *J. Am. Pharm. Assoc.* (1947) p. 16.

Contraction of Isopropanol on Mixing with Water

Weight %	Mols %	% Volume Contraction
100.0	100	00
98.4	95	.13
96.8	90	.36
94.9	85	.57
93.0	80	.79
90.8	75	1.01
88.6	70	1.23

86.0	65	1.43
83.3	60	1.65
80.2	55	1.85
77.0	50	2.05
73.2	45	2.20

Refractive Indices Isopropanol and water at 20°C.*

% Isopropanol by Vol.	N^{20}_{D}	d^{20}_{20}
2.85	1.3335	0.9962
3.56	1.3340	.9952
4.95	1.3375	.9888
10.08	1.3392	.9866
20.08	1.3478	.9755
29.83	1.3542	.9654
40.00	1.3590	.9520
50.15	1.3632	.9345
60.10	1.3678	.9137
69.99	1.3712	.8900
80.00	1.3745	.8640
90.01	1.3769	.8338
94.97	1.3770	.8160
99.50	1.3775	.7953

Ethanol		*Isopropanol*	
Spec. Grav. 15.5/15.5°C.	Ind. Refra. 20°C.	Spec. Grav. 15.5/15.5°C.	Ind. Refra. 20°C
.7961	1.3618	.7940	1.3775
.8160	1.3635	.7953	1.3775
.8337	1.3643	.8160	1.3770
.8499	1.3650	.8338	1.3769
.8637	1.3648	.8491	1.3758
.8776	1.3640	.8640	1.3745
.8899	1.3633	.8773	1.3730
.9021	1.3623	.8900	1.3712
.9132	1.3615	.9023	1.3695
.9239	1.3600	.9137	1.3678
.9340	1.3585	.9243	1.3658
.9436	1.3565	.9345	1.3632
.9518	1.3545	.9434	1.3612
.9590	1.3523	.9520	1.3590
.9656	1.3492	.9594	1.3567
.9708	1.3460	.9654	1.3542
.9759	1.3432	.9710	1.3510
.9811	1.3400	.9755	1.3478
.9865	1.3370	.9810	1.3435
.9904	1.3350	.9866	1.3392
.9929	1.3341	.9888	1.3375
.9948	1.3335	.9913	1.3358
.9958	1.3333	.9952	1.3340
		.9962	1.3335

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* From Bennett & Garratt, *Perfum. and Ess. Oil. Rec.*, **16,** 18 (1925).

Constant Boiling Mixtures of Isopropanol

	% by Wt.		% by Wt.	B.P. (°C)
Isopropanol	55.0	Acetonitrile (CH_3CN)	45.0	75.0
“	32.4	Benzene	67.6	71.9
“	8.1	Carbon disulfide	91.9	44.6
“	18.0	Carbon tetrachloride	82.0	67.0
“	4.2	Chloroform	95.8	60.8
“	66.5	Chloropicrin	33.5	82.0
“	36.0	1,3-Cyclohexadiene	64.0	70.4
“	32.8	Cyclohexane	67.2	68.6
“	36.0	Cyclohexene	64.0	71.0
“	27.6	Dichlorobromomethane	72.4	78.0
“	22.9	Ethyl acetate	77.1	74.8
“	45.0	Ethylene dichloride	55.0	74.0
“	22.2	*n*-Hexane	77.8	61.0
“	33.0	Isobutyl bromide	67.0	75.5
“	17.1	Isobutyl chloride	82.9	63.8
“	76.5	Isobutyl iodide	23.5	81.8
“	52.3	Isopropyl acetate	47.7	80.1
“	10.0	Isopropyl ether	90.0	64.9
“	30.0	Methyl ethyl ketone	70.0	77.3
“	3.1	Methyl iodide	96.9	42.3
“	28.2	Methyl propionate	71.8	77.0
“	16.0	*n*-Propyl bromide	84.0	65.2
“	3.9	*n*-Propyl chloride	96.1	45.8
“	80.6	Tetrachloroethylene	19.4	81.7
“	28.0	Trichloroethylene	72.0	74.0
“	68.6	Toluene	31.4	80.6
“	87.7	Water	12.3	80.4

Typical Properties of Isopropanol

	Anhydrous	91% (88% by wt.)
Boiling point	82.4°C	80.4°C
Freezing point	−85.8°C	
Specific gravity	$0.7874\ \frac{20^\circ\mathrm{C}}{20^\circ\mathrm{C}}$	$0.8158\ \frac{20^\circ\mathrm{C}}{20^\circ\mathrm{C}}$
Weight per gallon	6.56 lb. (20°C)	6.82 lb. (20°C)
Refractive index	1.3776 (20°C)	1.3769 (20°C)
Surface tension	21.7 dynes/cm. (20°C)	
Viscosity	0.0215 poise (24.4°C)	0.0227 poise (24.4°C)
Vapor pressure	31.6 mm. Hg (20°C)	35 mm. (20°C)
Specific heat	0.677 cal./g. (30°C)	0.740 cal./g. (30°C)
Flash-point	14.5°C (58.1°F)	16.7°C (62°F)
Heat of combustion	475 kg. cal./mole	
Heat of fusion	21.4 cal./g.	
Latent heat of evaporation	159.4 cal./g. at B.P.	
Electrical conductivity	35×10^{-7} recip. ohm (25°C)	

Typical specifications of 91% grade

Acidity (as acetic)	0.002%
Color	Water-white
Dilution with water	Clear

Distillation range	Not below 79.5°C Not over 80.7°C
Dryness (19 parts naphtha dilution)	Cloudy
Evaporation rate at 35°C	
5% Evap.	2–4 min.
25% “	10–15 “
50% “	20–25 “
75% “	35–40 “
90% “	45–50 “
95% “	50–55 “
100% “	55–60 “
Non volatile matter	Not more than 0.005 g per 100 cc
Odor	Mild
Odor residual	None
Residue on evaporation	1.0 mg per 100 cc
Specific gravity at 20/20°C	0.8175–0.8190
Water content	12.5% by Wt. (max.)
Weight per gallon at 20°C	6.812 lbs.

Typical specifications of 99% Grade

Acidity (as acetic acid)	Not more than 0.002%
Color	Water-white
Distillation range	81°–83°C
Dryness (19 parts naphtha)	Clear
Evaporation Rate at 35°C	
5% Evap.	2–4 min.
25% “	10–15 “
50% “	20–25 “
75% “	35–40 “
90% “	40–45 “
95% “	45–50 “
100% “	50–55 “
Flash point (Tag Closed Cup)	54°C
Nonvolatile Matter	0.005 g per 100 cc. (max.)
Residue (mg/100 cc maximum)	1.0
Specific gravity at 20/20°C	0.785 to 0.787
Specific heat at 20°C	0.595 cal./g
Surface tension at 5°C	22.8 dynes/cm
at 20	21.7 “
at 50	19.3 “
Thermal conductivity at 30°C	0.000367
Vapor pressure at 0°C	7.6 mm
10	15.9 “
40	105.6 “
50	176.8 “
90	1020.7 “
20	32.5 “
30	58.8 “
60	288.5 “
70	454.8 “
80	691.8 “
Viscosity at 20°C	0.0243 poise
Weight per gallon at 20°C	6.55 lbs.

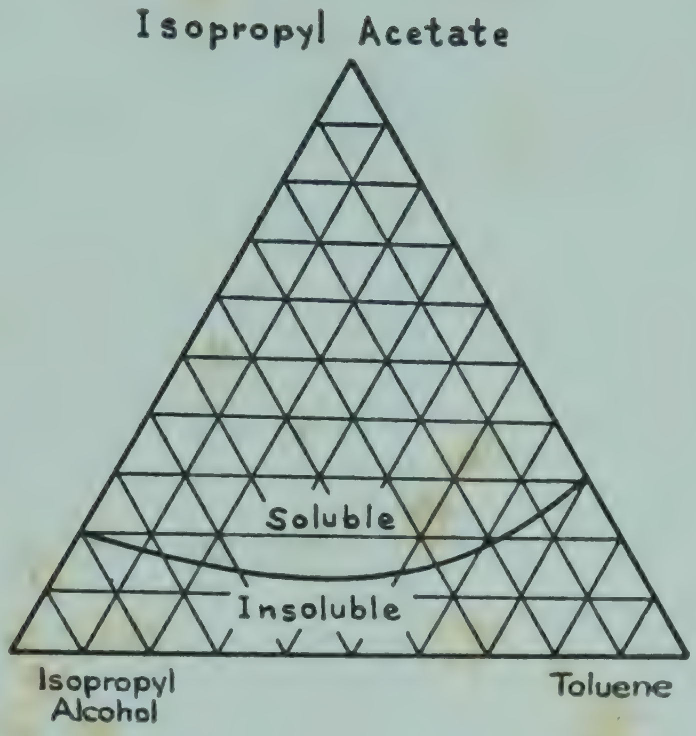

FIGURE 11.24.
Solubility of $\frac{1}{2}$-sec. Nitrocellulose.[4]

TABLE 11.6. MIXTURES OF ISOPROPANOL AND ACETONE

ISOPROPYL AL, R % BY WT.	HEAT OF MIXING, CAL. PER MOL. OF MIXTURE 20°C.	DENSITY, 25°C.	REFRACT. INDEX, n_d^{25}	TOTAL VAPOR PRESSURE, 25°C	VISC., 25°C
0	—	.7855	1.3555	226.5	.00308
15.65	−190	.7832	1.3578	—	.00347
16.56	−196	.7831	1.3579	221.6	.00349
30.00	−316	.7818	1.3604	—	.00389
30.89	−320	.7816	1.3605	—	.00395
46.34	−362	.7805	1.3634	—	.00486
49.72	−388 (max.)	.7806	1.3641	167.2	.00507
49.85	−385	.7807	1.3641	—	.00513
66.90	−343	.7801	1.3672	139.6	.00703
67.41	−357	—	—	—	—
67.61	−338	—	—	—	—
81.70	−236	.7804	1.3708	—	.01071
85.37	−197	.7805	1.3711	—	.01187
100.00	—	.7813	1.3743	44.3	.02020

Mixtures of Isopropanol and Ethyl Alcohol

% ETHYL ALCOHOL	n_d^{25}	VISCOSITY, 25°C	% EtOH IN VAPOR AT 25°C
0	1.3750	.02048	0
17.23	1.3721	.01796	21.4
33.60	1.3697	.01607	41.2
49.87	1.3675	.01445	59.3
66.89	1.3646	.01299	73.5
83.61	1.3622	.01182	87.5
100.00	1.3595	.01080	100.

TABLE 11.7. COMPARATIVE SOLUBILITIES IN ISOPROPANOL AND ETHANOL*

OILS	ISOPROPANOL	ETHANOL 90%	ISOPROPANOL 50%	ETHANOL 45%
Almond	All	All	20.0	22.0
Ambrette seed	1.0	1.0	—	—
Anise	5.0	3.0	250.0	250.0
Bay	All	1.0	100.0	200.0
Bergamot	1.0	1.0	200.0	400.0
Bergamot, terpeneless	1.0	All	200.0	180.0
Cajuput	3.0	5.0	170.0	190.0
Cananga	1.0	1.5	250.0	500.0
Caraway	All	1.0	50.0	195.0
Cardamoms	All	1.0	50.0	80.0
Cassin	All	1.0	50.0	150.0
Cedarwood	6.0	12.0	200.0	500.0
Celery	All	10.0	250.0	—
Cinnamon bark	2.0	0.3	110.0	92.0
Cinnamon leaf	All	All	50.0	100.0
Citronella, Ceylon	2.4	1.0	220.0	200.0
Citronella, Java	All	1.0	100.0	165.0
Clove	All	All	50.0	80.0
Cognac	All	All	210.0	225.0
Coriander	0.5	0.5	180.0	200.0
Dill	All	3.0	90.0	100.0
Eucalyptus	2.6	5.0	170.0	210.0
Fennel	2.0	1.0	240.0	200.0
Geranium, African	All	All	50.0	200.0
Gingergrass	1.6	1.0	130.0	125.0
Juniper	2.4	4.0	200.0	210.0
Lavender, French	All	2.5	30.0	100.0
Lavender, terpeneless	2.0	All	110.0	90.0
Lavender, spike, Fr.	All	2.0	50.0	150.0
Lemon	2.0	4.0	100.0	200.0
Lemon, terpeneless	2.0	All	180.0	170.0
Lemongrass	2.0	14.0	45.0	85.0
Limes, Dist.	2.4	4.5	55.0	75.0
Lignaloe	All	2.0	50.0	100.0
Neroli, Bigarad	2.4	2.0	110.0	100.0
Nutmeg:	2.0	3.0	145.0	130.0
Orange, bitter	10.0	10.0	140.0	150.0
Orange, bitter, terpeneless	2.0	6.0	220.0	210.0
Orange, sweet	10.0	10.0	200.0	210.0
Orange, sweet, terpeneless	1.5	6.0	245.0	250.0
Orris, concrete	1.0	1.0	—	—
Otto Rose (filtered)	All	All	200.0	250.0

TABLE 11.7—*Continued*

OILS	ISOPROPANOL	ETHANOL 90%	ISOPROPANOL 50%	ETHANOL 45%
Palmarosa	1.7	3.0	80.0	100.0
Patchouli	4.0	10.0	250.0	500.0
Pepper	All	7.0	300.0	—
Peppermint, Amer.	All	All	200.0	150.0
Peppermint, Jap.	All	2.0	50.0	180.0
Petitgrain	2.3	2.0	95.0	100.0
Petitgrain, terpeneless	2.4	All	160.0	150.0
Pimento	1.6	All	60.0	50.0
Pine, sylvest	0.5	3.0	250.0	—
Rose, Femelle	1.0	1.0	90.0	100.0
Rosemary, Fr.	All	2.0	45.0	100.0
Rosemary, Fr., terpeneless	2.0	All	110.0	100.0
Rue	2.0	All	125.0	120.0
Sage	2.6	2.0	110.0	100.0
Sage, Sclaree	2.0	2.0	—	—
Sandal, E. I.	2.7	5.0	80.0	160.0
Sassafras	3.4	3.0	220.0	200.0
Spearmint	1.8	1.0	—	—
Thyme, rouge	All	1.0	100.0	200.0
Vetivert	2.0	2.0	—	—
Ylang	turbid	0.75	40.0	100.0

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* The indication is for one part by weight or volume of substance in the stated figures which are the solvent, *e.g.*, anise 1 in 5. Blank = less than 1 in 1000. "All" = in at least 0.1 of its own weight or volume.

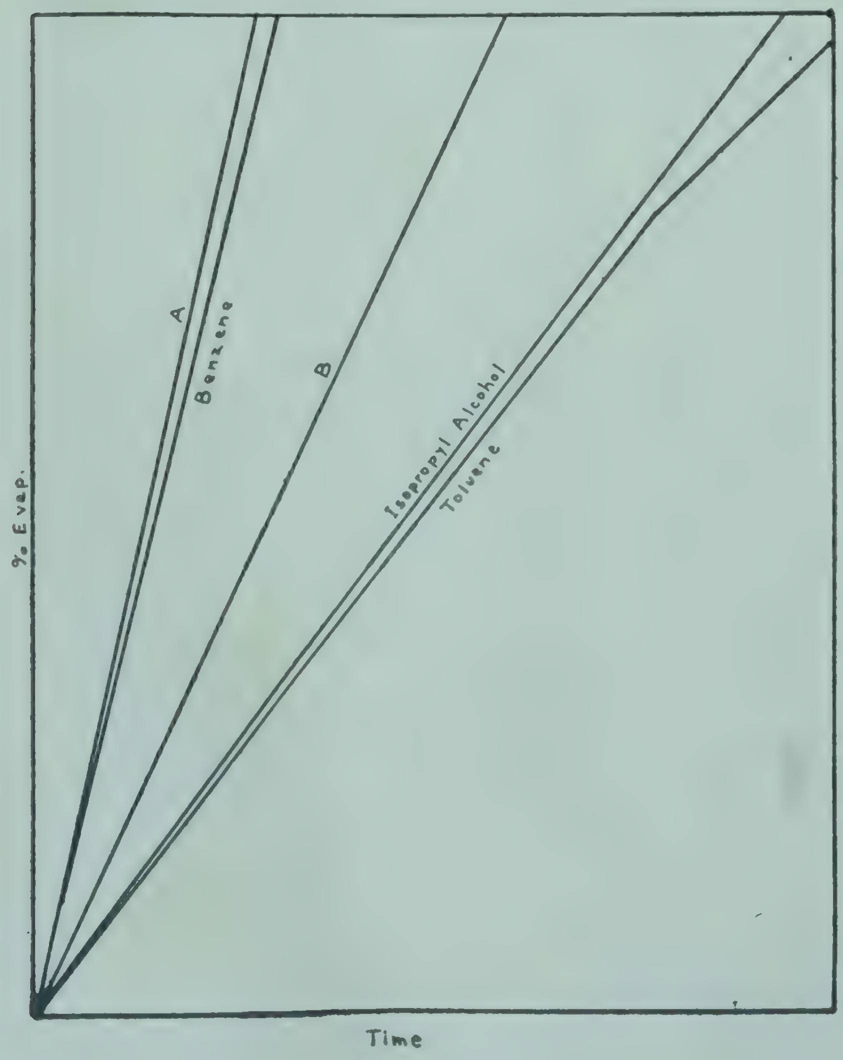


FIGURE 11.25.
Evaporation Rates:
A = 75 Benzene, 25 Isopropyl Alcohol
B = 48 Toluene, 52 Isopropyl Alcohol
Constant Evaporating Mixtures.
Room Temperature.

Table 11.8. Solubilities of Synthetic Perfume Materials in Ethanol and Isopropanol

	ISOPROPANOL	ETHANOL 90%	ISOPROPANOL 50%	ETHANOL 45%
Acetic ether	All	All	All	All
Acetophenone	All	All	7.0	8.0
Amyl acetate	All	All	20.0	21.0
Amyl alcohol	All	All	2.5	3.0
Amyl valer	All	All	170.0	180.0
Anethol	1.0	2.0	85.0	100.0
Anisic ald	All	All	10.0	30.0
Benzaldehyde	1.4	1.0	7.0	15.0
Benzyl acet	All	1.0	10.0	35.0
Benzyl alc	1.0	1.0	1.5	2.0
Benzyl benz	2.0	2.0	—	—
Benzyl butyrate	All	All	65.0	70.0
Benzyl formate	All	All	28.0	29.0
Benzyl valer	All	All	125.0	130.0
Benzylidene acetone	0.2	0.25	9.0	8.0
Bornyl acet	All	All	200.0	200.0
Bromstyrol	2.0	5.0	250.0	500.0
Butyl acet	All	All	8.0	9.0
Cinnamic alc	All	All	7.0	7.5
Citral	1.8	1.0	—	—
Citronellal	2.8	1.0	—	—
Citronellol	All	1.0	20.0	40.0
Citronellyl acet	All	All	300.0	330.0
Coumarin	5.0	6.0	25.0	35.0
Ethyl cinnamate	All	All	130.0	140.0
Eugenol	1.2	All	10.0	8.0
Formic ether	All	All	1.0	1.0
Geraniol	All	1.0	20.0	50.0
Geranyl acet	All	All	750.0	800.0
Geranyl butyrate	All	All	550.0	560.0
Heliotropin	0.3	2.5	30.0	33.0
Ionone	All	All	50.0	110.0
Ionone alpha	All	All	30.0	60.0
Iso-eugenol	All	All	10.0	30.0
Iso-butyl acetate	All	All	11.0	10.0
Jasmin art	1.0	All	70.0	70.0
Linalol	2.0	1.0	20.0	18.0
Linalyl acet	All	1.0	50.0	200.0
Linalyl butyrate	All	All	170.0	180.0
Methyl acetophenone	All	1.0	12.0	14.0
Methyl anisate	1.5	2.0	30.0	32.0
Methyl anthranilate	7.5	5.0	25.0	20.0
Methyl benzoate	1.0	All	—	—
Methyl salicyl	All	1.0	70.0	166.0
Mirbane	All	All	30.0	75.0

TABLE 11.8—*Continued*

	SOPROPANOL	ETHANOL 90%	ISOPROPANOL 50%	ETHANOL 45%
Musk ambrette	55.0	100.0	—	—
Musk xylol	200.0	250.0	—	—
Neroli art	3.0	2.0	320.0	300.0
Nerolin	50.0	50.0	600.0	666.0
Oenanthic ether	All	All	—	—
Phenyl acetic acid	0.8	0.75	1.75	1.4
Phenyl acetic ald	All	All	—	—
Phenyl ethyl alc	All	All	3.0	4.5
Phenyl oxide	2.0	5.0	100.0	300.0
Phenyl propyl alc	All	All	250.0	260.0
Rhodinol	2.0	1.0	170.0	160.0
Safrol	5.0	10.0	150.0	300.0
Salicyl amyl	1.0	3.0	200.0	500.0
Styrolyl valer	All	All	140.0	150.0
Terpineol	All	1.0	10.0	30.0
Terpinyl acet	All	1.0	—	—
Terpinyl prop.	All	All	100.0	110.0
Vanillin	1.25	2.5	5.0	10.0

TABLE 11.9. MIXTURES OF ISOPROPANOL AND ALDEHYDES

Isopropyl Alcohol and Acetaldehyde				Isopropyl Alcohol and Heptaldehyde			
% Aldehyde	n_d^8	% Aldehyde	n_d^8	% Aldehyde	n_d^{25}	% Aldehyde	n_d^{25}
0	1.38516	70.6	1.36864	0	1.36994	62.6	1.39945
13.3	1.38391	74.2	1.36552	11.7	1.38113	69.8	1.40350
33.6	1.38247	81.0	1.36044	17.2	1.38381	80.6	1.40577
42.6	1.38008	92.1	1.35193	20.0	1.38640	89.4	1.40765
52.6	1.37640	95.8	1.34941	40.0	1.39318	91.9	1.40835
64.4	1.37218	100.	1.34445	50.4	1.39699	100.	1.40884

Isopropyl alcohol does not appear to form compounds (hemiacetals) with the above aldehydes, as does ethyl alcohol.

***n*-Butanol.** (*n*-Butyl alcohol, Butanol-1) ($CH_3CH_2CH_2CH_2OH$). *n*-Butanol was first isolated from fusel oil by Wurtz in 1852. It did not achieve importance until World War I, when in the acute need for acetone a special fermentation method was developed which exceeded all expectations by yielding two pounds of butanol for every pound of acetone. Today about half the *n*-butanol production is made synthetically from acetaldehyde or ethanol.

This fourth member of the series of primary monohydric alcohols is a water-white, combustible but not flammable liquid having a mild alcoholic

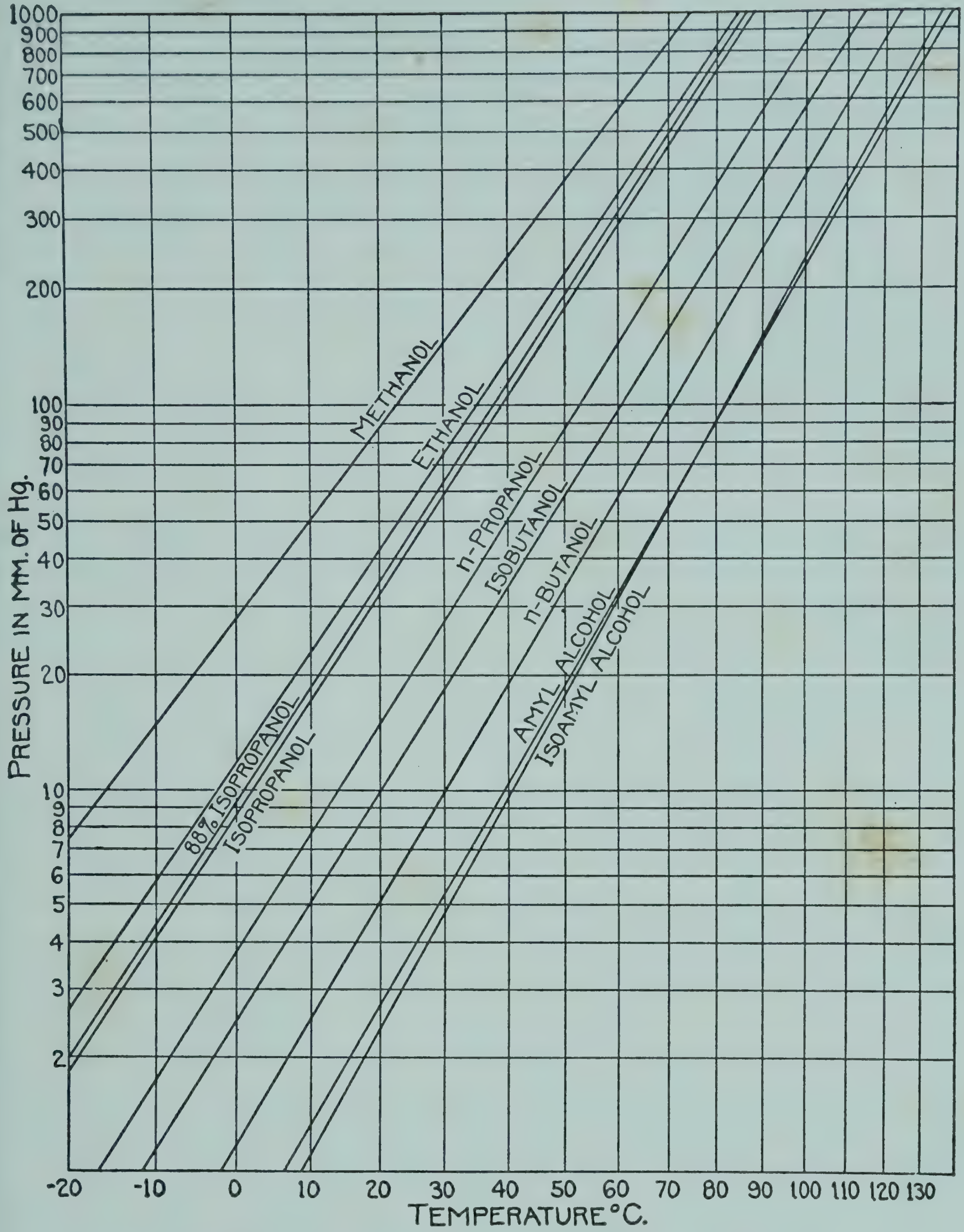


FIGURE 11.26. Vapor Pressure of Alcohols at Various Temperatures.

odor and ranging in purity from 98 per cent to better than 99%. It is miscible with most solvents and is used as a blending medium for many immiscible liquids. It is a solvent for alkaloids, camphor, capsicum, resorcinol, dyes, vegetable oils such as castor and linseed oils, gums, waxes, ethyl cellulose, calcium and magnesium resinates, natural resins, such as congo, dammar, elemi, kauri, manila, sandarac, and shellac, such synthetic resins as ester gum, alkyd resins and urea-born aldehyde resins. It possesses

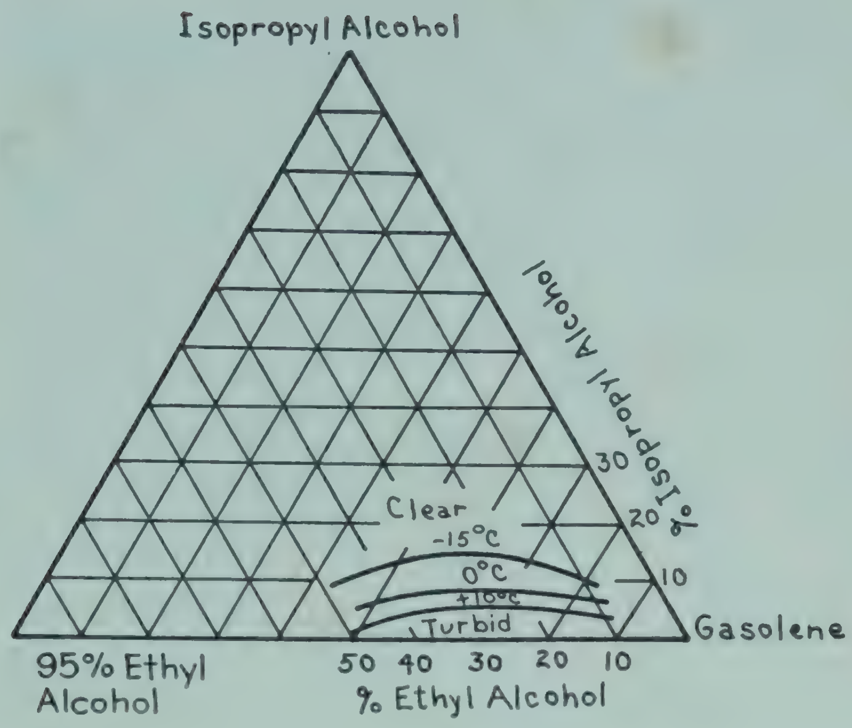

Isopropyl Alcohol
% Isopropyl Alcohol
30
20
10
Clear
-15°C
0°C
+10°C
Turbid
Gasolene
95% Ethyl Alcohol
50 40 30 20 10
% Ethyl Alcohol

FIGURE 11.27.
Miscibility of Isopropanol, 95% Ethyl Alcohol and Gasoline $\left(d\,\frac{15}{15}\,0.7231\right)$.[5]

latent properties for nitrocellulose and when mixed with aromatic hydrocarbon diluents, or alkyl acetates, butanol will dissolve many of the cellulose esters and ethers.

Butanol is used as an adjunct for active solvents for the purpose of enhancing their solvent properties. It is used extensively as a "medium boiler" in the manufacture of pyroxylin lacquers for its solvency, its power to impart flow, gloss, blush prevention, and to lower viscosity. It is particularly valuable when used in synthetic resin formulations because it imparts good leveling qualities, reduces viscosity, prevents blushing, and improves flow and working qualities. As shown in Table 11.10, important

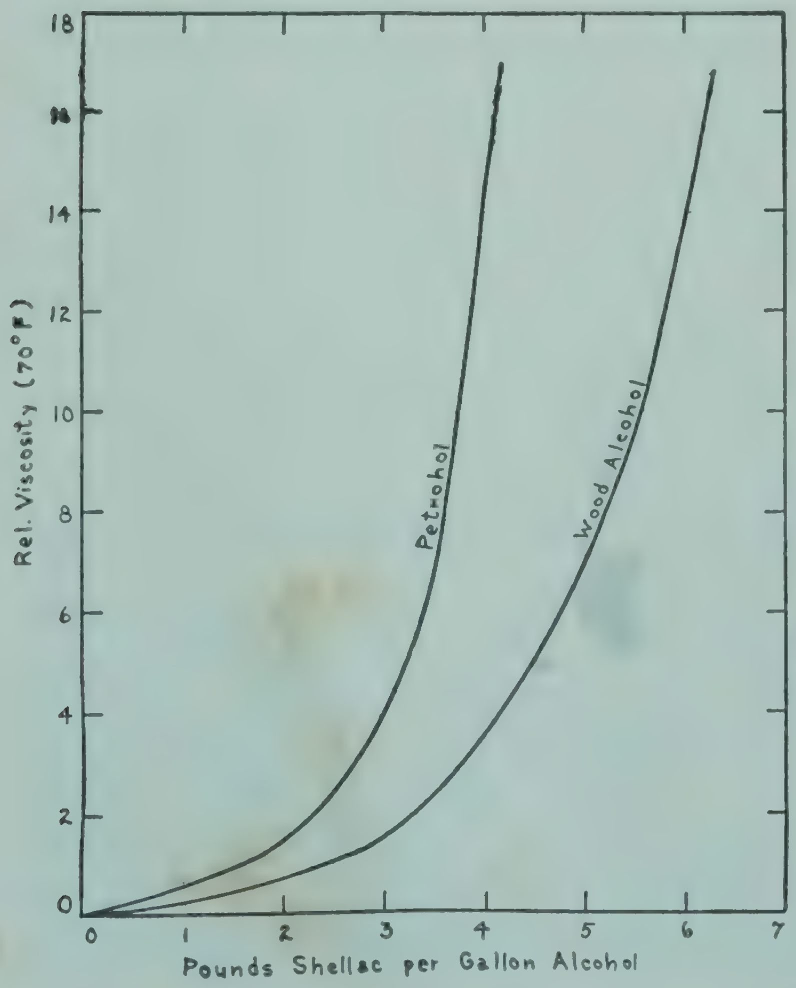


FIGURE 11.28.
Viscosity of Shellac Solutions at Room Temperature.

TABLE 11.10. ALLOCATIONS OF NORMAL BUTYL ALCOHOL*
Jan. 1, 1944–June 30, 1945 (Thousands of lbs.)

USE	TOTAL		JANUARY 1–JUNE 30, 1945	JULY 1–DECEMBER 31, 1944	JANUARY 1–JUNE 30, 1944
	Amount	Per cent			
Total allocations	256,090	100.0	88,099	86,026	81,965
Direct military[1]	2	0.0	2	0	0
Export	23,578	9.2	6,018	10,975	6,585
Other essential	232,510	90.8	82,079	75,051	75,380
Chemical manufacture	151,272	59.1	54,316	49,480	47,476
Butyl acetate	75,060	29.3	25,687	22,746	26,627
Dibutyl phthalate	48,032	18.8	18,991	17,100	11,941
Other butyl derivatives[2]	28,180	11.0	9,638	9,634	8,908
Lacquer solvents	39,268	15.3	14,580	12,536	12,152
Aircraft coatings	21,771	8.5	8,940	7,388	5,443
Ammunition coatings	2,600	1.0	935	605	1,060
Textiles and leather	794	0.3	256	186	352
Dyes and penetrants	1,478	0.5	580	505	393
Other protective coatings	12,625	5.0	3,869	3,852	4,904
Other uses	41,970	16.4	13,183	13,035	15,752
Resins and plastics	7,103	2.8	2,804	2,109	2,190
Photography and films	2,205	0.9	750	685	770
Hydraulic brake fluids	2,867	1.1	1,385	678	804
Oil additives	686	0.3	207	265	214
Miscellaneous uses and small orders[3]	29,109	11.3	8,037	9,298	11,774

[1] End-use data not available.

[2] Includes normal butyl alcohol used to make butyl cellosolve and butyl amines.

[3] Includes normal butyl alcohol used to make cellulose acetate sheets, insect repellents, medicinals, flotation reagents, butyric acid, cleaners and dehydrating agents, and for research.

* "Facts for Industry," Bureau of the Census.

industrial derivatives of butanol include the plasticizers dibutyl pththalate, dibutyl sebacate and the lacquer solvent, butyl acetate.

Constant-boiling Mixtures of n-Butanol

	% by Wt.		% by Wt.	B.P. (°C)
n-Butanol	44.8	*n*-Butyl acetate	55.2	113.5
“	24.0	*n*-Butyl formate	76.0	105.8
“	63.0	Chlorobenzene	37.0	107.2
“	9.8	Cyclohexane	90.2	79.8
“	19.9	Ethyl isobutyrate	80.1	108.5
“	30.8	Methyl isovalerate	64.2	113.0
“	32.0	Perchloroethylene	68.0	110.0
“	33.5	Tetrachloroethylene	66.5	110.0
“	32.1	Toluene	67.9	105.5
“	62.7	Water	37.3	92.3

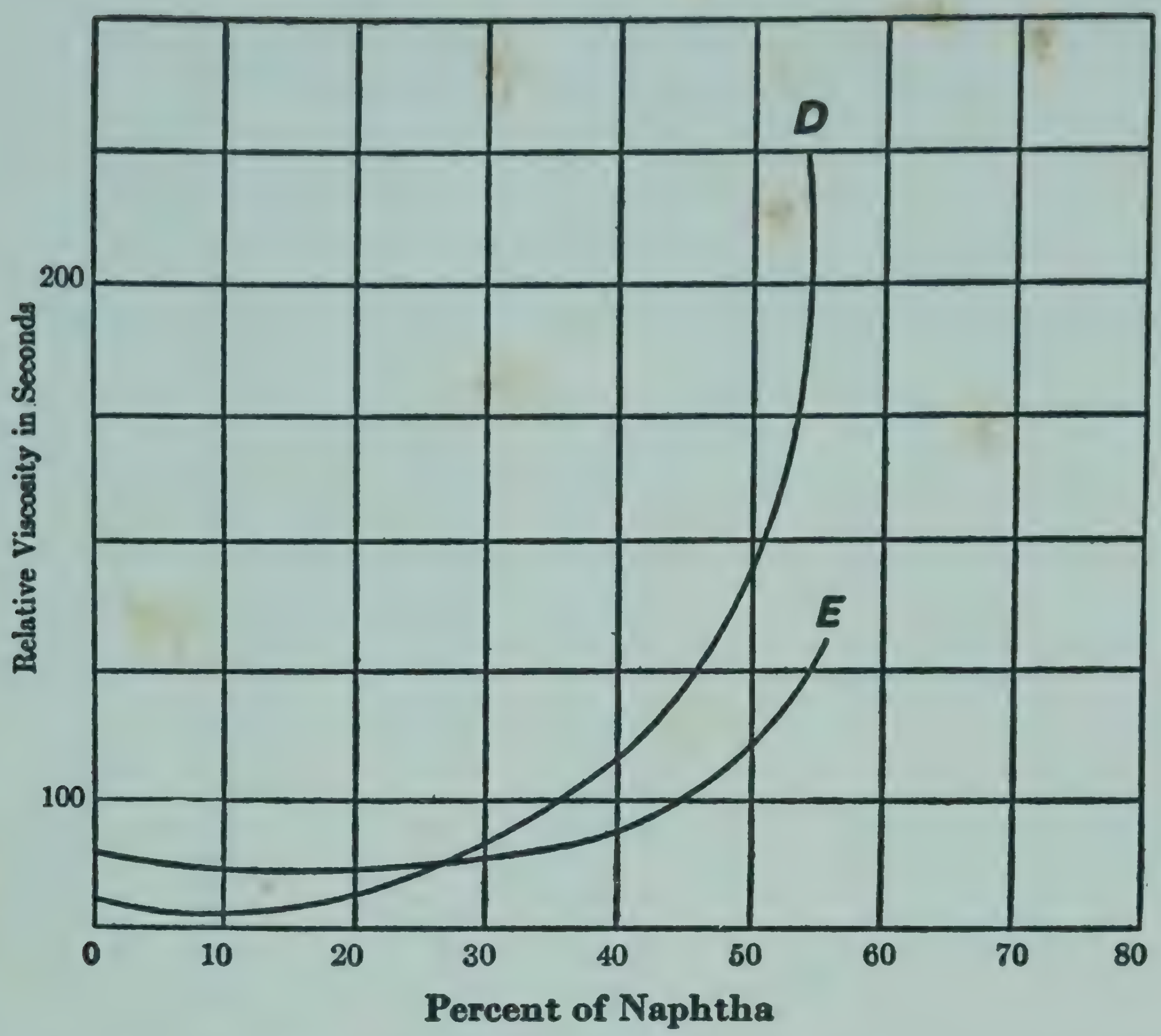


FIGURE 11.29. The effect of increasing proportions of naphtha on the viscosity of 10% solutions of nitrocellulose in: Butyl Acetate (Curve D); A Mixture of Butyl Acetate (67%) and Butanol (33%) (Curve E).

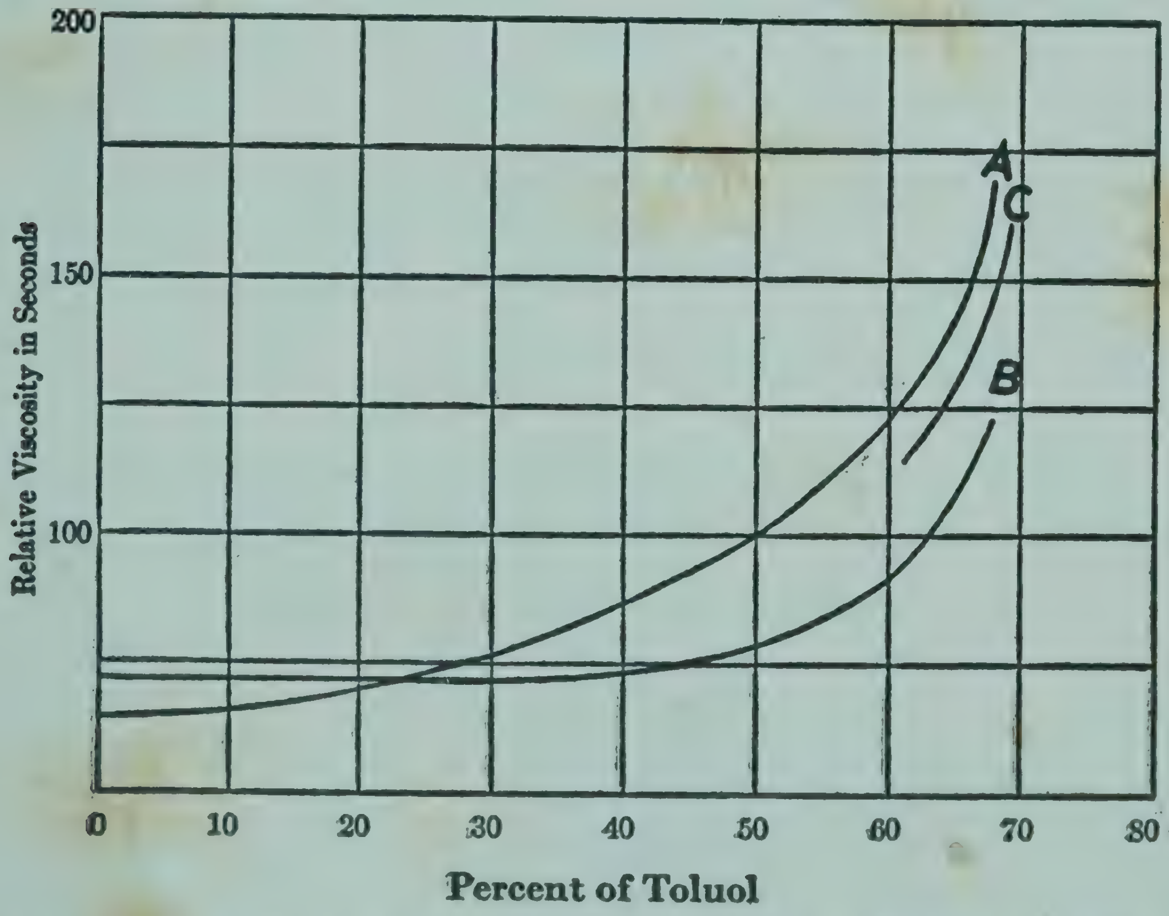


FIGURE 11.30. The effect of increasing proportions of Toluol on the viscosity of 10% solutions of nitrocellulose in: Butyl Acetate (Curve A); A Mixture of Butyl Acetate (67%) and Butanol (33%) (Curve B); A Mixture of Butyl Acetate (60%) and Ethyl Acetate (40%) (Curve C).

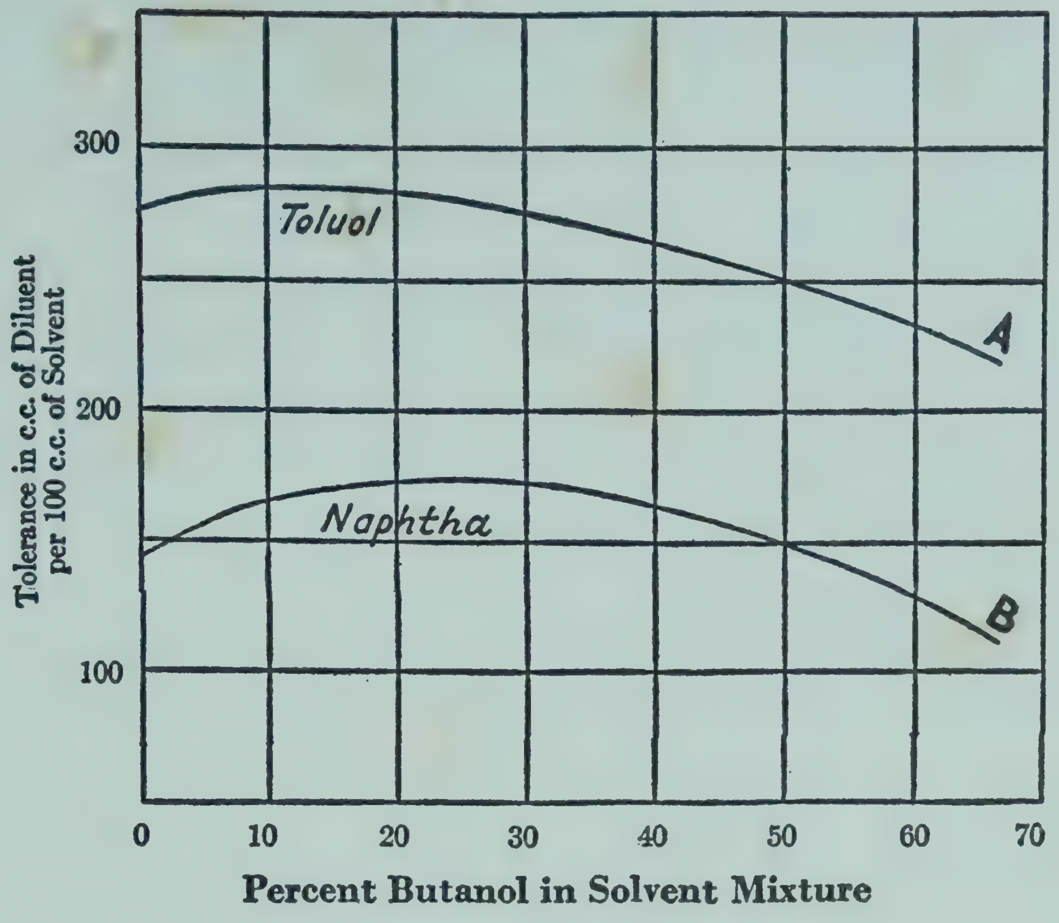


FIGURE 11.31.

Typical Properties and Specifications

Boiling point	117.7°C
Coefficient of cubical expansion	0.00052 per °F 0.00093 per °C
Critical temperature	28.7°C
Critical pressure	48.4 atm
Dielectric constant at 25°C	16.1
Electrical conductivity at 26°C	3.6×10^{-7} recip. ohm
Evaporation rate at 95°F (in minutes)	
5%	2½
25%	13¼
50%	26¾
75%	44½
90%	59½
95%	67
Flash point (ASTM Open Cup)	43.9°C
Freezing point	−89.8°C
Heat of combustion	639 kg cal./mol
Heat of fusion	29.9 cal./g
Latent heat of vaporization at B.P.	141.3 cal./g
Melting point	−79.90°C
Refractive Index at 25°C	1.3974
Specific gravity at 20/20°C	0.810 to 0.813
Specific heat from 20 to 114°C	0.689
Vapor pressure at 20.0°C	4.3 mm
40.0	18.6 "
60.0	59.2 "
75.0	131.3 "

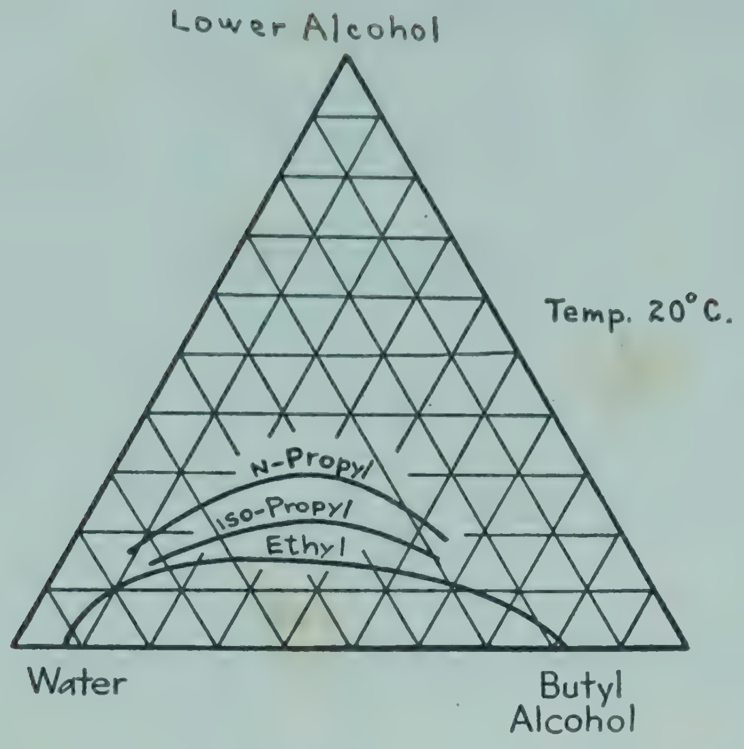
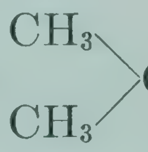


FIGURE 11.32. Miscibility of Certain Lower Alcohols with Water and Butyl Alcohol[5] (Int. Critical Tables III, 412).

Viscosity (absolute) at 20°C	29.48 millipoises
Weight per gallon	6.76 lbs.
Acidity, as acetic acid	0.01% max.
Boiling range at 760 mm	115°–118°C
Color	Water-white
Dryness at 20°C	Miscible with 19 vol. 60° Bé. gasoline
Iron	29.9 cal./g
Nonvolatile matter	0.005 mg/100 cc (max.)
Residue on Evaporation	0.005% by wt. (max.)
Solubility in acid	Completely soluble in 96% sulfuric acid
Solubility in water	10% by wt. (max.)
Solubility of water in butanol at 25°C	17.12% by vol.



Isobutyl Alcohol $\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CHCH_2OH$ (isopropyl carbinol, 2-methyl propanol 1) is a water-white, flammable liquid obtained commercially as a by-product of the high-pressure methanol synthesis and more recently by the oxidation of natural gas hydrocarbons.

Boiling point	107–108°C
Flash point	22°C
Melting point	−108°C
Refractive index	1.397
Specific gravity	0.8057

Isobutyl alcohol resembles the normal isomer in its industrial applications.

sec.-**Butanol** (methyl ethyl carbinol, butanol-2) ($CH_3—CHOH—CH_2—CH_3$). The synthetic production of secondary butanol is a recent development in the field of alcohols. This medium-boiling alcohol is made from butylene obtained in the cracking of petroleum. This olefin is reacted with

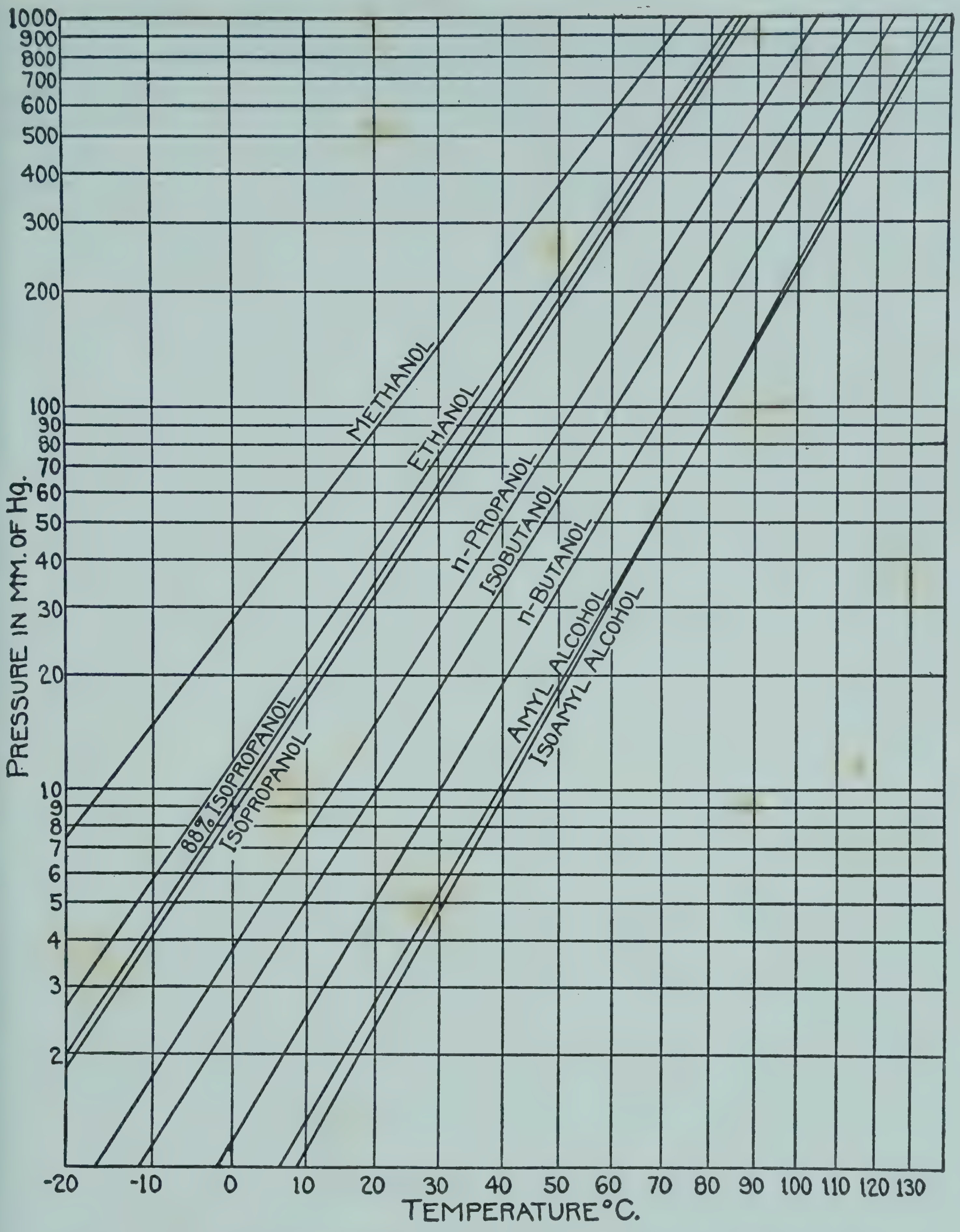


FIGURE 11.33. Vapor Pressure of Alcohols at Various Temperatures.[6]

sulfuric acid to form butyl hydrogen sulfate, which is then treated with steam to form secondary butanol.

It is a water-white, flammable liquid with a boiling range between that of anhydrous ethanol and *n*-butanol. It is miscible with alcohols, esters, ethers, hydrocarbons, aromatic hydrocarbons, and most organic solvents. It will dissolve such resins as ester gum, kauri, shellac, sandarac, mastic, elemi, as well as linseed and castor oils. It is a latent solvent for

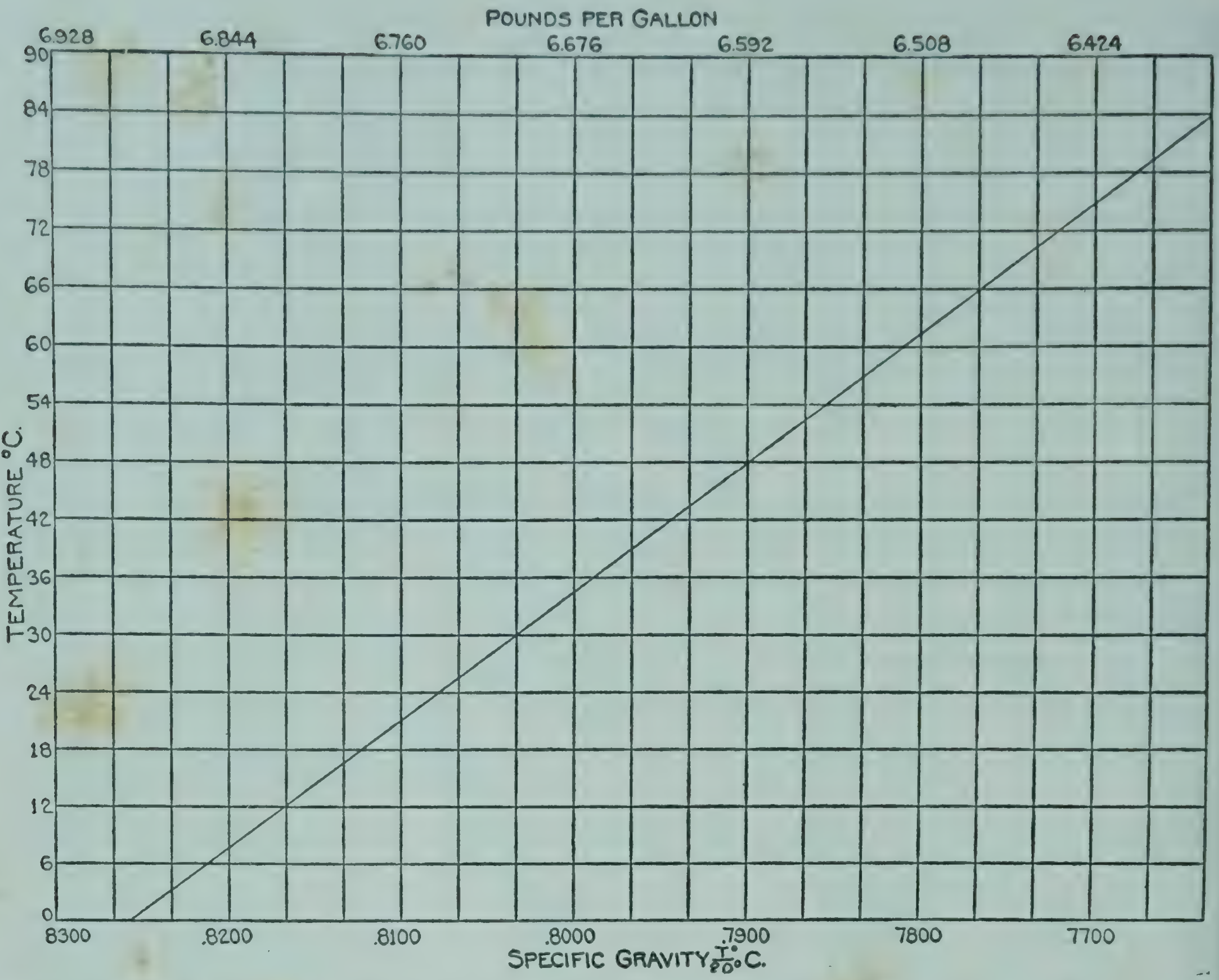


FIGURE 11.34. Specific Gravity and Weight per Gallon of *n*-Butanol at Various Temperatures.[6]

cellulose esters and has an evaporation rate which lies between that of *n*-butyl acetate and toluene. It is therefore used in lacquers and lacquer thinners to promote good flow and leveling. Like *n*-butanol it may be used as an antifoaming agent, as a dispersant for dyes, in the preparation of penetrating oils and greases, in polishes, cleaning solutions, as a coupling agent, and as a dehydrating medium. The bulk of *sec*-butanol production is converted into the solvent, methyl ethyl ketone.

Typical Properties and Specifications

Boiling point at 760 mm		99.5°C
Coefficient of expansion		0.000545 per °F 0.00097 per °C
Color		Water-white
Constant-boiling mixture	*sec*-Butanol	72.3 B.P. 87.5°C
	Water	27.7
Flash point (Tag Closed Cup)		73°F
Freezing point		−114.7°C
Latent heat of vaporization at 98.1°C		134.4 cal/g
Solubility in water		20.5% by wt.

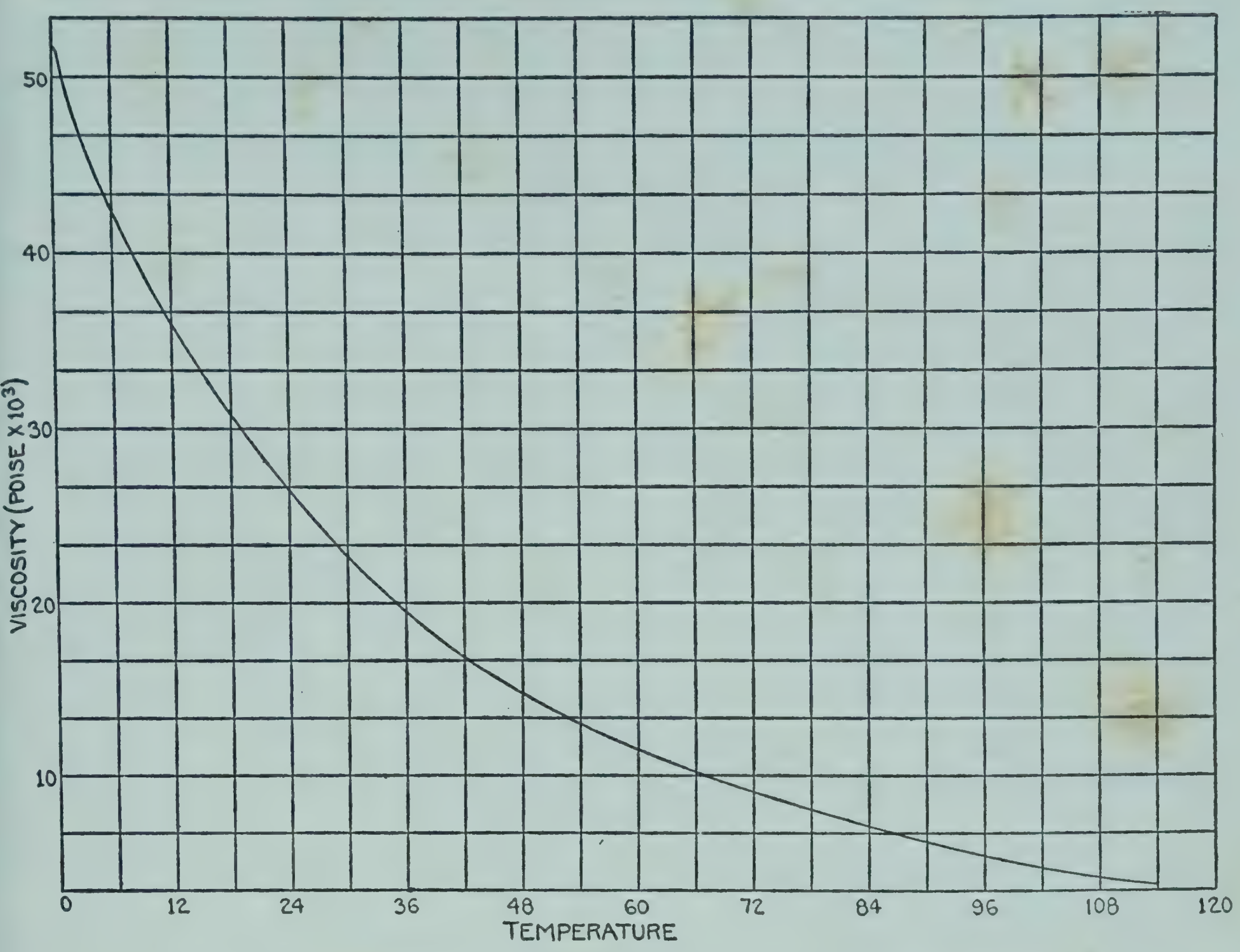


FIGURE 11.35. Viscosity of n-Butanol at Various Temperatures.[6]

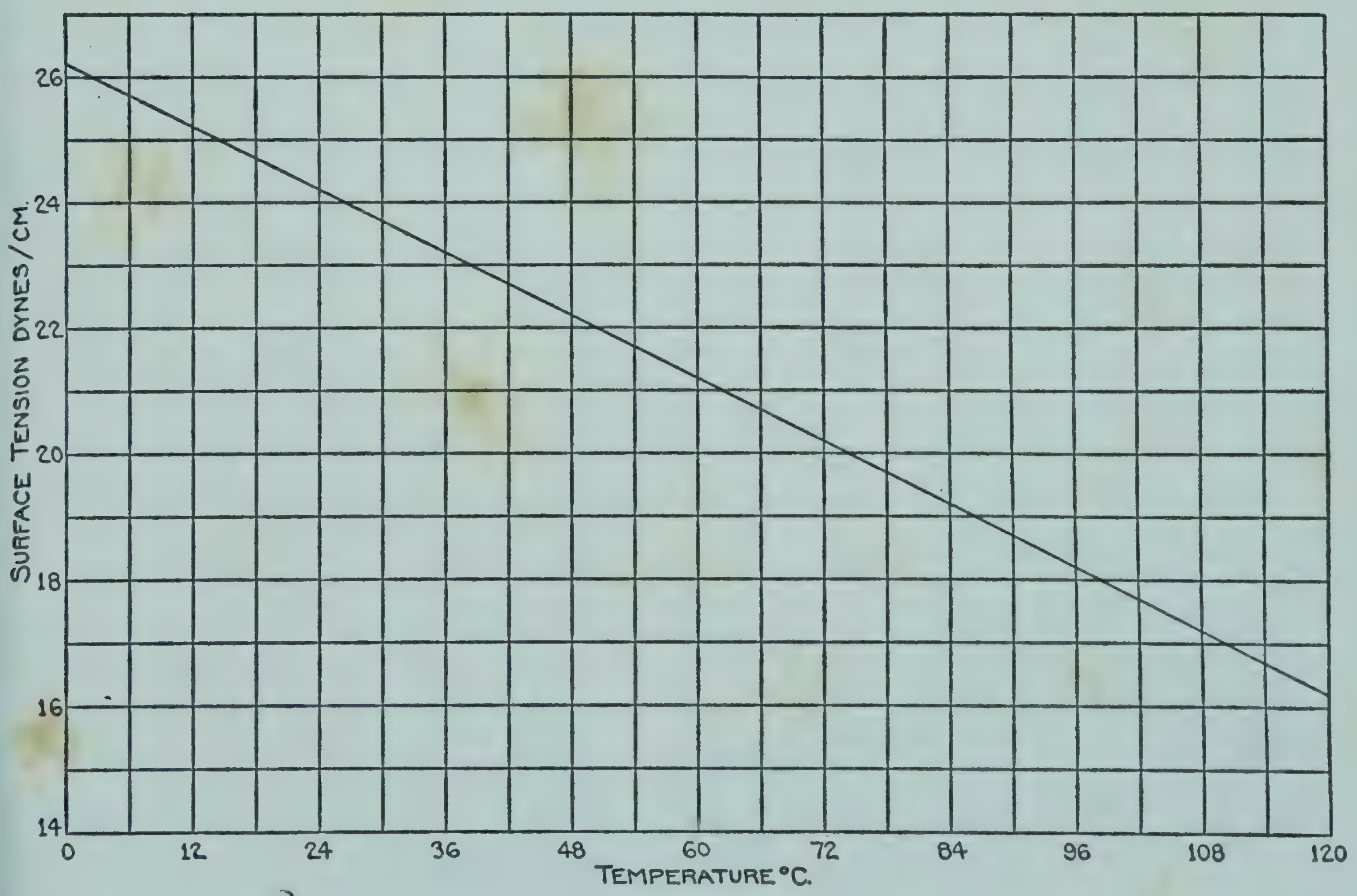


FIGURE 11.36. Surface Tension of n-Butanol at Various Temperatures.[6]

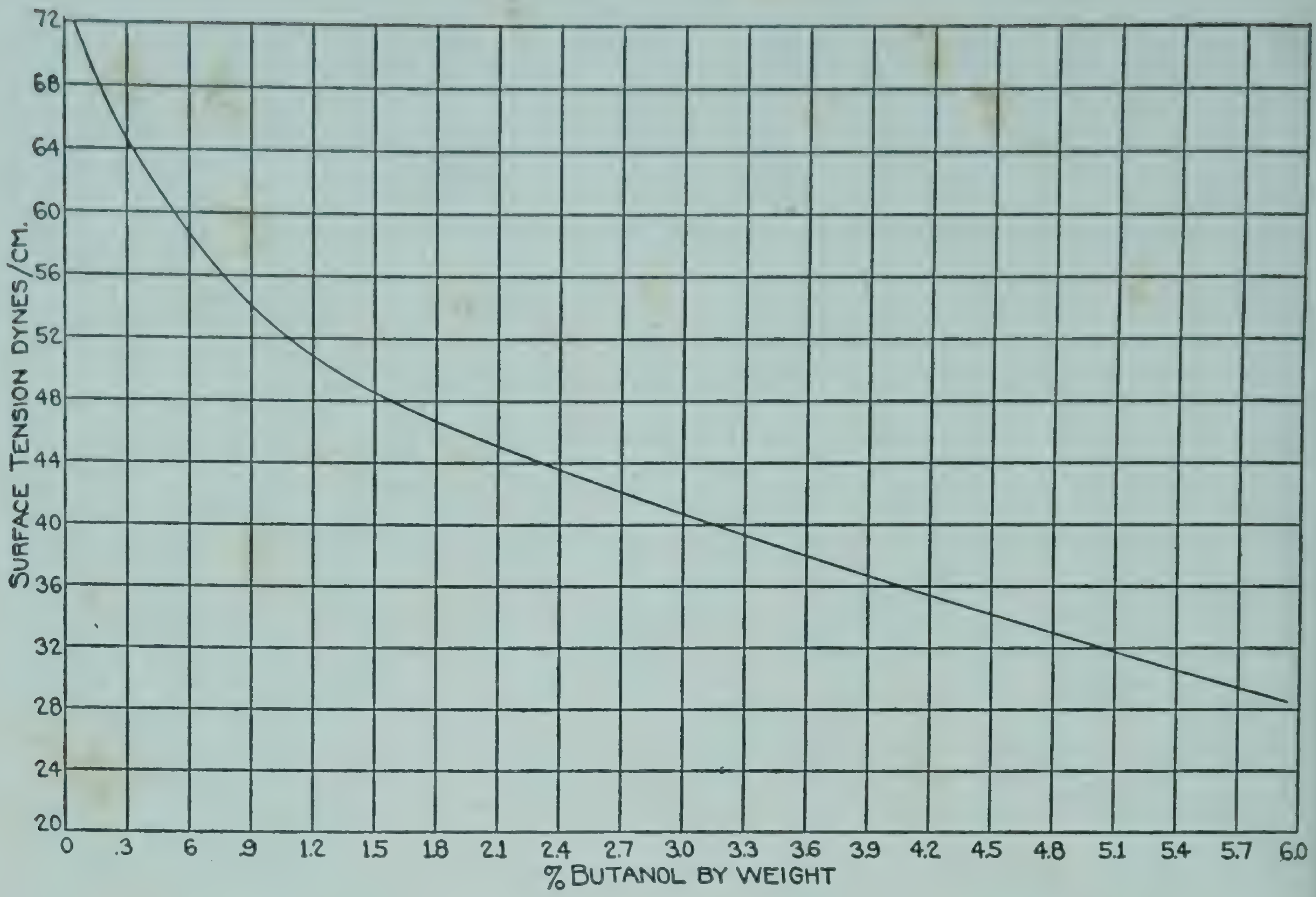


FIGURE 11.37. Surface Tension of Aqueous Solutions (at 25°C.) of *n*-Butanol.[6]

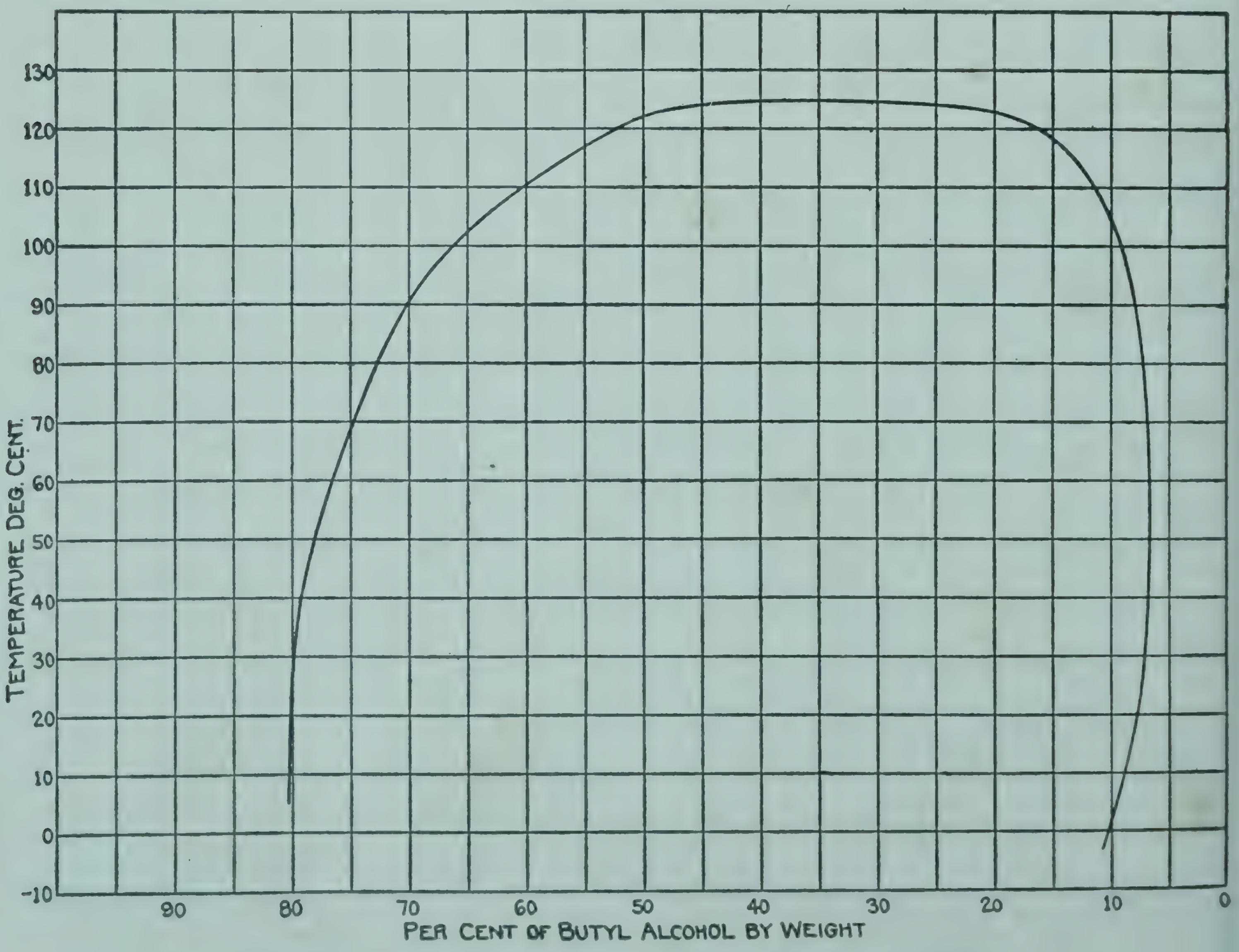


FIGURE 11.38. Solubility of *n*-Butanol in Water.[6]

Specific gravity at 15/15°C	0.8103–0.8140
Refractive index	1.3971
Specific heat	0.67 cal/g
Surface tension 10°C	23.5 dynes/cm
Evaporation rate at 35°C	
5% Evap.	2–5 Minutes
25% "	15–20 "
50% "	32–37 "
75% "	52–57 "
90% "	65–70 "
95% "	70–75 "
Total	75–80 "
Vapor pressure at 0°C	2.5 mm
10	5.7 "
20	12.1 "
30	23.9 "
Weight per gallon at 20°C	6.73 lbs.
Acidity, as acetic acid	0.004% max.
Distillation range	Below 95°C None Above 101°C None More than 90% distills over between 97°C and 101°C
Dryness	Clear on dilution with 19 parts naphtha
Non volatile matter	4 mg per 100 ml max.
Purity	98% by wt. min.
Residue	0.005 g per 100 cc max.

tert.-**Butanol** (2-Methyl-propanol-2 *tert.*-Butyl alcohol) $[(CH_3)_3COH]$. Commercially tertiary butanol is a water-white, hygroscopic, crystalline solid of 99 per cent purity and containing less than 0.004 per cent non-volatile matter. When heated above its melting point, 25.6°C, it becomes a colorless liquid having a mild camphor-like odor.

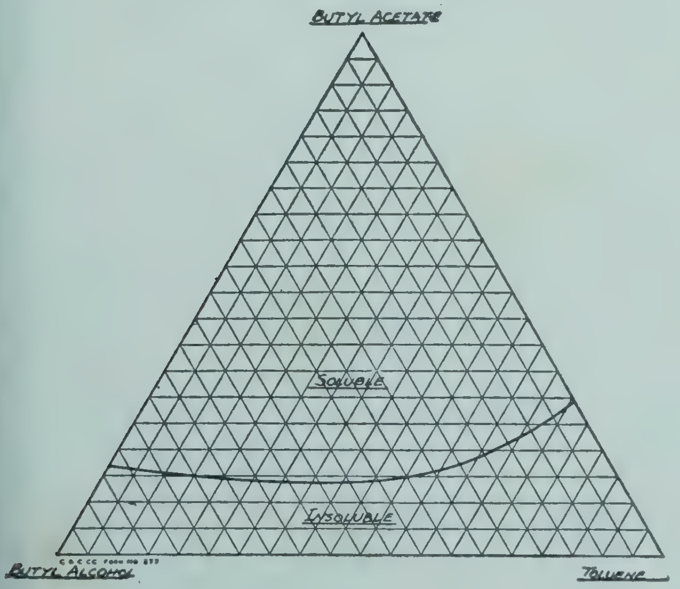


Figure 11.39. Solubility of ½-Second R.S. Nitrocellulose in Mixtures of Butyl Acetate, Butyl Alcohol, and Toluene.[6]

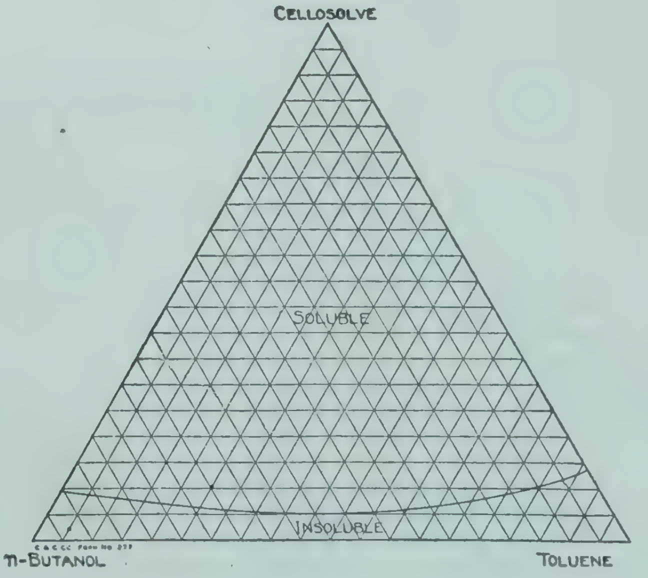


Figure 11.40. Solubility of ½-Second R.S. Nitrocellulose in Mixtures of "Cellosolve," Butyl Alcohol and Toluene.[6]

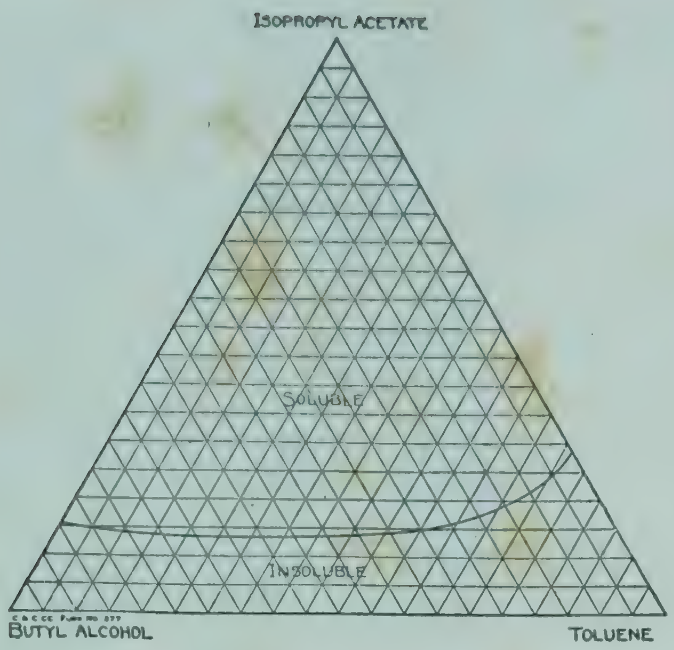


FIGURE 11.41. Solubility of ½-Second R.S. Nitrocellulose in Mixtures of Isopropyl Acetate, Butyl Alcohol, and Toluene.[6]

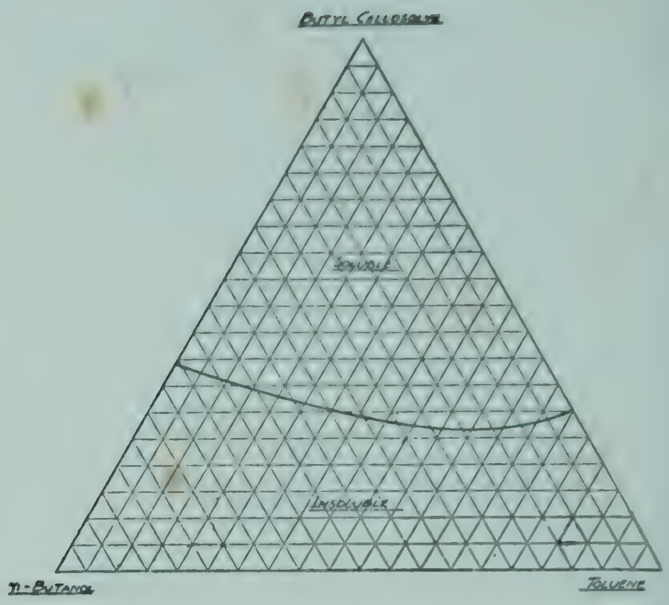


FIGURE 11.42. Solubility of ½-Second Nitrocellulose (Dry) in Mixtures of Butyl "Cellosolve," Butyl Alcohol, and Toluene.[6]

It is completely miscible with alcohols, esters, ethers, aromatic and aliphatic hydrocarbons, most organic solvents, and water. The fact that it mixes with water in all proportions, when in a liquid state, distinguishes it from its isomers; *tert.*-butanol is used as a blending agent because it is very stable and water-miscible, and has mutual solvency. It is also used for the removal of water from substances, in the extraction of drugs, in the manufacture of perfumes, and in purifying chemicals by recrystallization.

Typical Properties and Specifications

Boiling point at 760 mm	82.4°C
Coefficient of expansion	0.000740 per °F
Color	Water-white
Critical temperature	235°C
Flash point (Tag Closed Cup)	48°F
Freezing point (first needle)	Above 20°C
Heat of combustion (1) at const. vol.	634.0 cal.
Heat of fusion	21.00 cal.
Latent heat of evaporation	130.6 cal./g
Latent heat of fusion at 25.6°C	21.0 cal./g
Melting point	25.6°C
" " 99.4%	23.0°C
Solubility in water	Miscible without turbidity with 19 volumes of 60° Bé. gasoline at 20°C
Specific gravity at 25/25°C	0.783
Refractive index	1.38779
Surface tension at 34.5°C	19.45 dynes/cm
Vapor pressure at 20°C	30.6 mm
30	57.3 "
40	103.0 "

Viscosity at 30°C		0.033498
Weight per gallon at 25°C		6.52 lbs. (approx.)
Acidity, as acetic acid		0.003% max.
Distillation range (ASTM)	Below 78°C	None
	Above 85°C	None
	More than 95% distills over between 81° and 83°C	
Purity		99% *tert.* butanol

AMYL ALCOHOLS

Both synthetic and fermentation products are commercially available. The wartime end use pattern for amyl alcohols is shown in Table 11.11.

Refined Fusel Oil ($C_5H_{11}OH$). Fusel oil is obtained as a by-product in the production of ethanol by molasses fermentation. This alcohol is then treated chemically and distilled, thus yielding the refined product. Refined fusel oil is a blend of a number of amyl alcohols, with a preponderance of isoamyl alcohol, and with small amounts of lower alcohols, esters, furfural and pyridine. It is a water-white liquid miscible with aromatic hydrocarbons and oils. It is a solvent for camphor, alkaloids, natural gums and resins, and such synthetic resins as the alkyds, maleics, phenolics, and urea-aldehyde. When fusel oil is used together with active solvents, the mixture will dissolve acetyl and nitrocellulose, and a mixture of refined fusel oil and benzene or methyl or ethyl acetate will dissolve many of the cellulose ethers.

Fusel oil has the distinction of being the oldest lacquer solvent. This is due to its unusual blending properties which impart flow and gloss to lacquers. For this reason it is largely consumed in protective coating formulation, as well as in the manufacture of amyl compounds, pharmaceuticals, flavors, and xanthates.

Typical Properties and Specifications

Coefficient of expansion	Per 1°F	0.00051
	Per 1°C	0.00092
Color		Water-white
Dryness	Miscible without turbidity with 20 volumes 60° Bé. gasoline at 20°C	
Evaporation Rate at 95°F (in minutes):	5%	3½
	25%	17
	50%	36½
	75%	64¾
	90%	90¼
	95%	103½
Flash point		108°F (approx.)
Residue on evaporation		None

Solubility of water alcohol at 25°C	9.9% by vol.
Specific gravity at 20/20°C	0.811–0.815
Weight per gallon at 20°C	6.76 lbs. (approx.)
Acidity (as acetic acid)	0.01% max.
Boiling range: Below 100°C	None
Below 110	Not over 10%
Below 120	Not over 30%
Below 130	At least 90%
Above 145	None
Non volatile matter	0.005 g per 100 cc (max.)

Refined Amyl Alcohol. Refined amyl alcohol has the approximate composition of 85 per cent isoamyl alcohol and 15 per cent active amyl alcohol. It is obtained from fusel oil and is a water-white liquid with a mild odor.

$CH_3—CH(CH_3)—CH_2—CH_2OH$	Isoamyl alcohol
$CH_3—CH_2—CH(CH_3)—CH_2OH$	Active amyl alcohol

Typical Properties and Specifications

Coefficient of expansion Per 1°F	0.00051
Per 1° C	0.00092
Color	Water-white
Dryness	Miscible without turbidity with 20 vols. 60° Bé. gasoline at 20°C
Flash point	111°F
Specific gravity at 20/20°C	0.811–0.815
Weight per gallon at 20°C	6.76 lb. (approx.)
Acidity (as acetic acid)	0.02% (max.)
Distillation range	126–132°C
Nonvolatile matter	0.003 g per 100 cc (max.)

Table 11.11. Allocations of Amyl Alcohols (All Grades): April 1–June 30, 1945*
(Thousands of pounds mixed alcohols)

Use	Amount	Per cent
Total allocations	4,623	100.0
Amyl acetate (all grades)	[1]2,345	50.7
Lacquers and solvents[2]	1,279	27.7
Ore flotation reagents	418	9.0
Drugs and pharmaceuticals	235	5.1
Adhesives	180	3.9
Petroleum refining	44	1.0
Miscellaneous uses and small orders[3]	122	2.6

[1] Used in the production of penicillin (20%), lacquers (73%), and other uses.

[2] Includes methyl propyl ketone.

[3] Includes carburizing fluids, gum inhibitors, shoe preparations, electrical equipment uses, cleaners, and printing inks.

* "Facts for Industry," Bureau of the Census.

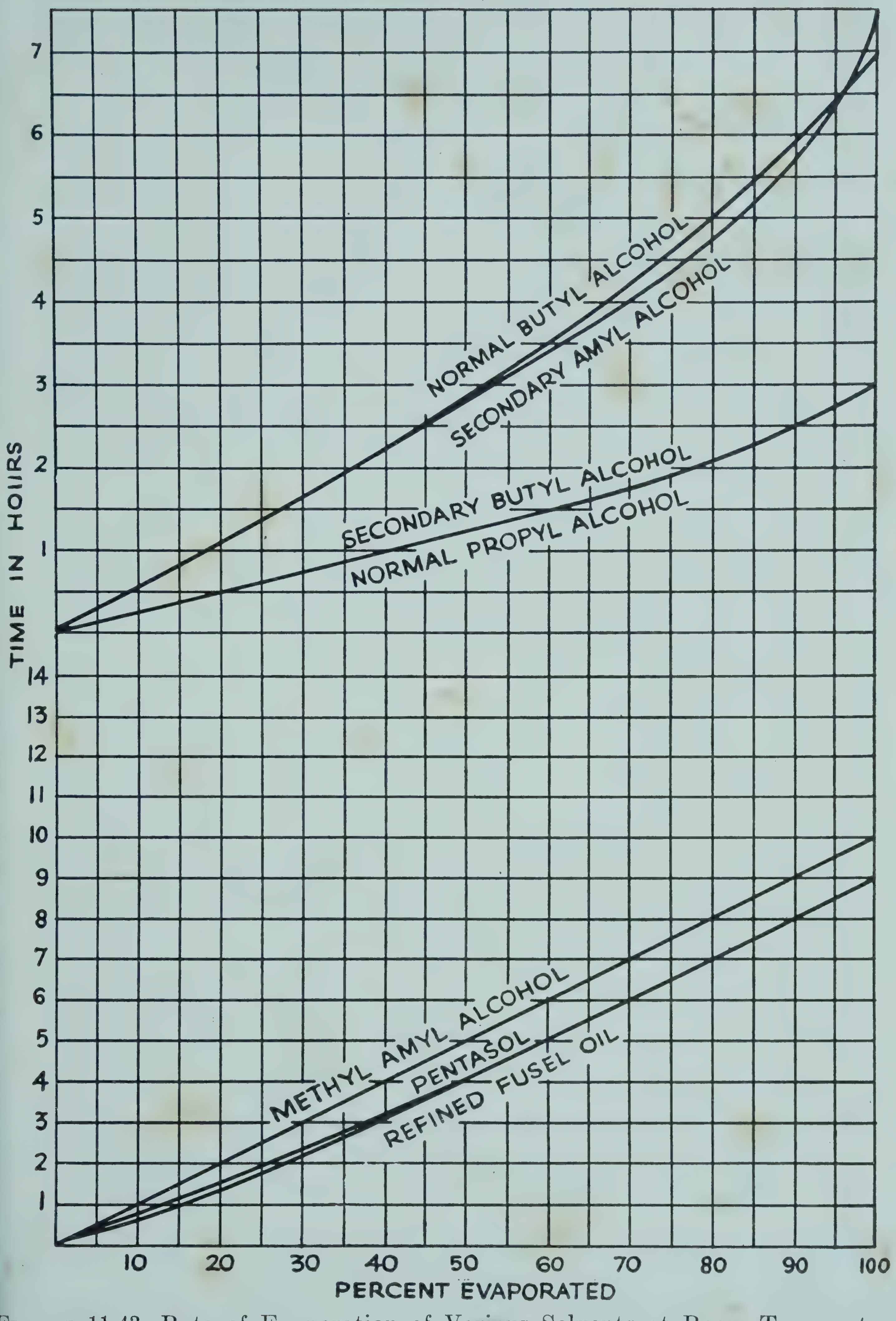


Figure 11.43. Rate of Evaporation of Various Solvents at Room Temperature.[30]

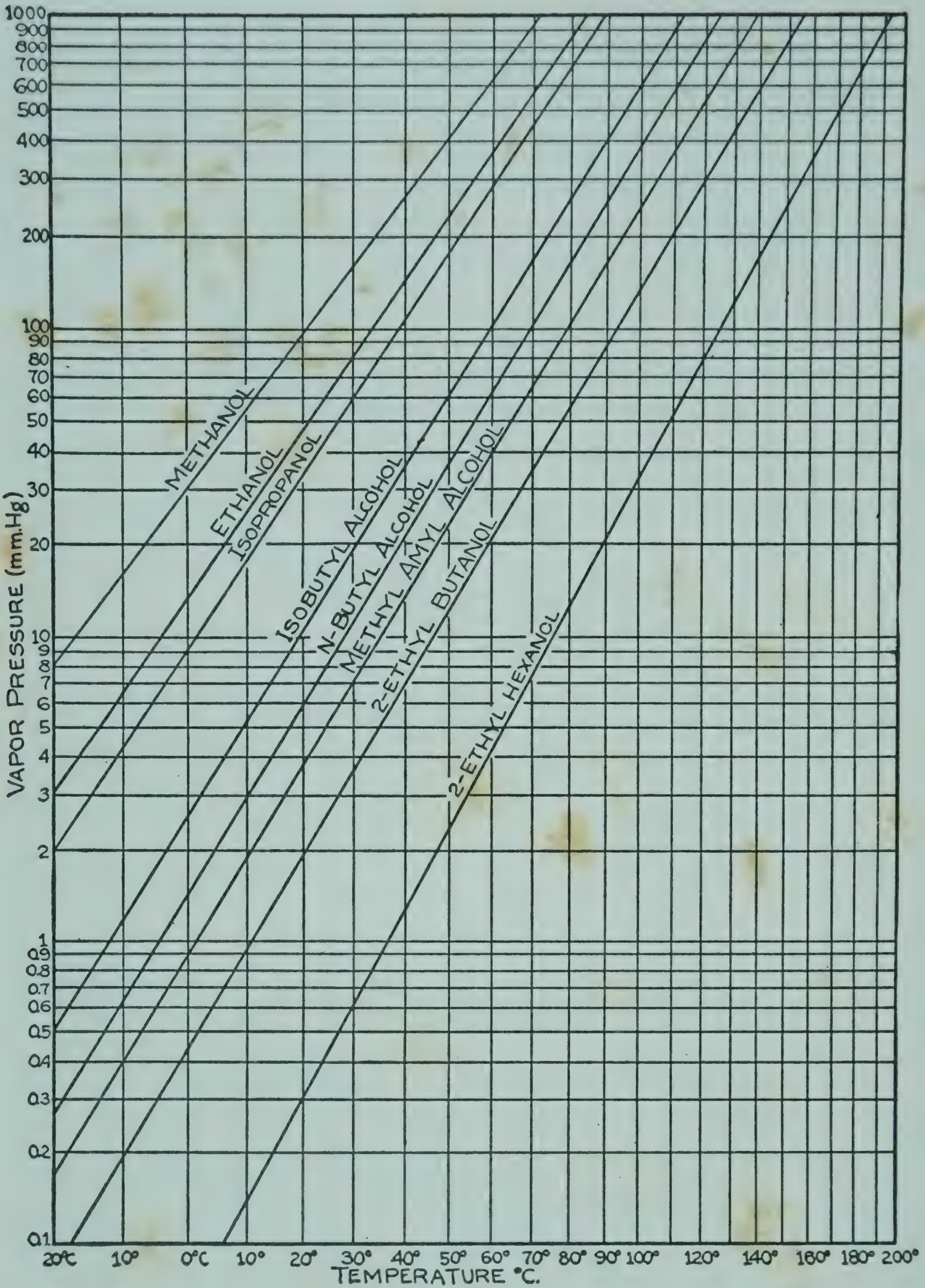


FIGURE 11.44. Vapor Pressure of Alcohols at Various Temperatures.[3]

Pentasol. Pentasol is a commercial grade of amyl alcohol produced synthetically from pentane. It is essentially a mixture of the isomeric amyl alcohols derived from normal and isopentane. The three primary alcohols are present in highest proportion. The following alcohols are present in Pentasol:

	B.P. (°C)
$CH_3CH_2CH_2CH_2CH_2OH$	137.9
$(CH_3)_2CHCH_2CH_2OH$	130.5
$CH_3CH_2CH(CH_3)CH_2OH$	128.0
$CH_3CH_2CH_2CHOHCH_3$	119.0
$CH_3CH_2CHOHCH_2CH_3$	115.6

It is a colorless liquid of mild odor, with practically no residual odor, and forms an azeotropic mixture with water. It is only slightly soluble in water, but is miscible with methanol, ethyl ether, ethyl acetate, acetone, aromatic and aliphatic hydrocarbons and vegetable oils. It is widely used in lacquer formulation as it imparts flow, gloss and blush resistance. Other uses for Pentasol are in hydraulic fluids, in the manufacture of xanthates, and as an antifoaming agent. The acetate of Pentasol is an important medium-boiling nitrocellulose lacquer solvent. One of the newer uses for Pentasol is as a solvent in urea-formaldehyde resin coatings.

Typical Properties and Specifications

Coefficient of expansion per °C	0.00099 at 10 to 35°C
Color	Water-white
Evaporation rate at 114.8°F (in minutes): 4.60	2.5%
9.25	50%
14.60	75%
22.75	100%
Fire point (Open cup)	120°F
Flash point (Open cup)	115°F
Heat of vaporization	99.4 cal./g (calc'd.)
Solubility in water	3.0% by vol.
Solubility water in solvent	8.4% by vol.
Specific gravity at 20/20°C	0.810–0.820
Refractive index at 20°C	1.4092
Specific heat	0.725 cal./g (approx.)
Surface tension	37.7 dynes/cm
Weight per gallon at 20°C	6.79 lbs.
Acidity (mg KOH per g)	0.06 max.
Distillation range: Initial boiling point	Not below 112°C
Not more than 5%	Below 118°C
Not more than 50%	Below 125°C
Not more than 85%	Below 130°C
Final boiling point	Not above 140°C
Nonvolatile at 100°C	0.005 g/100 cc max.

Primary *n*-Amyl Alcohol (Pentanol-1, *n*-butyl carbinol) [$CH_3 \cdot (CH_2)_3 \cdot CH_2OH$]. Primary normal amyl alcohol is a colorless liquid obtained from Pentasol. The commercial material contains small quantities of isobutyl carbinol and diamyl ether as impurities. It is slightly soluble in water but is almost completely soluble in methanol, ethyl ether, ethyl acetate, acetone, aromatic and aliphatic hydrocarbons, fixed oils, oleic and hot

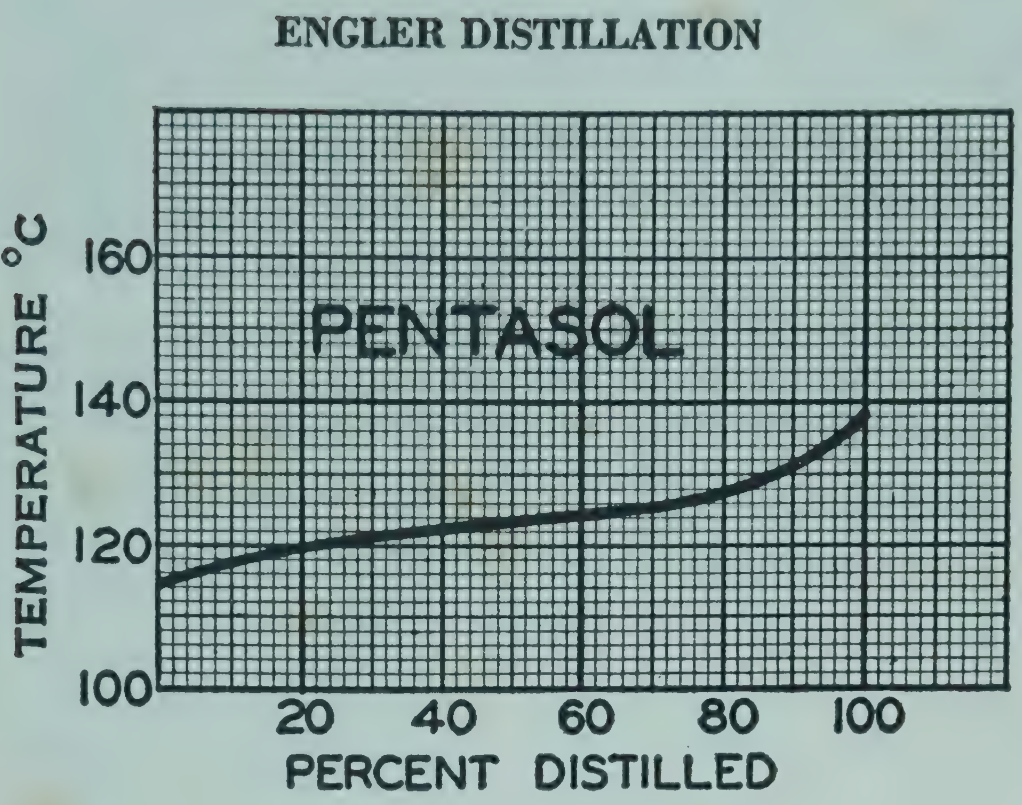


FIGURE 11.45.

stearic acids, hot paraffin and carnauba waxes, the latter two solidifying when cooled. It is used in the preparation of pharmaceuticals and other synthetic products.

Typical Properties and Specifications

Boiling point	137.9°C
Coefficient of expansion per °C	0.00092
Fire point (Open cup)	140°F
Flash point (Open cup)	185°F
Heat of vaporization	120.6 cal./g (calc'd.)
Melting point	−78.5°C
Specific gravity at 20/20°C	0.82
Refractive index at 20°C	1.4113
Specific heat	0.712 cal./g
Viscosity at 25°C	3.31 centipoises
60°C	1.33 "
Weight per gallon at 20°C	6.83 lbs.
Acidity (mg KOH per g)	0.06 (max.)
Distillation range	95% between 134.5–138.5°C
Nonvolatile at 100°C	0.003 g/100 cc (max.)

sec.-**Amyl Alcohol** (Pentanol-2, methylpropyl carbinol) ($CH_3CH_2CH_2$-$CHOHCH_3$). Pentanol-2 is a water-white liquid obtained from amylene, which in turn is obtained in the cracking of petroleum. It is used principally as a solvent in nitrocellulose lacquers and lacquer thinners.

Typical Properties and Specifications

Boiling point	119.5°C
Coefficient of expansion per 1°F	0.00053
per 1°C	0.00095

Color	Water-white
Flash point	121°F
Heat of vaporization	97.8 cal./g (calc'd.)
Nonvolatile at 100°C	0.003 g/100 cc (max.)
Specific gravity at 20°C	0.810–0.816
Solubility of water in solvent	8.2% by vol.
Evaporation rate at 90°F (in minutes): 5%	$2\frac{1}{4}$
25%	$11\frac{3}{4}$
50%	$24\frac{1}{4}$
75%	$38\frac{1}{4}$
90%	$50\frac{1}{4}$
95%	$56\frac{1}{2}$
Weight per gallon at 20°C	6.75 lbs.
Acidity (as acetic acid)	0.02% (max.)
Distillation range	105°–125°C
Purity	99% by wt. (min.)

*sec.-n-***Amyl Alcohol** (Pentanol-3, diethyl carbinol) ($CH_3CH_2CHOHCH_2CH_3$). Pentanol-3 is a water-white liquid containing small percentages of the isomeric higher and lower alcohols as impurities. It is slightly soluble in water but miscible with ether, benzene, and naphtha. Its most important use is in the manufacture of flotation agents for nonferrous ores.

Typical Properties and Specifications

Boiling point	115.6°C
Coefficient of expansion	0.00149 per °C
Color	Water-white
Distillation	95% between 113.6–117.6°C
Flash point (Open Cup)	100°F
Heat of vaporization	96.8 cal./g (calc'd.)
Freezing point	< -75°C
Specific gravity at 25/4°C	0.815
Refractive index at 20°C	1.4098
Viscosity at 25°C	4.12 centipoises
at 60°C	1.09 "
Weight per gallon at 20°C	6.83 lbs.
Acidity (as acetic acid)	0.06% (max.)
Nonvolatile at 100°C	0.003 g/100 cc (max.)

Isoamyl Alcohol (3-Methyl-1-butanol, primary isoamyl alcohol, isobutyl carbinol) [$CH_2(CH_3) \cdot CH_2CH_2 \cdot CH_2OH$]. Isoamyl alcohol is a water-white liquid containing small amounts of impurities, such as *sec.*-butyl carbinol and *n*-butyl carbinol. It is slightly soluble in water but miscible with ether, benzene, and naphtha. Use has been found for it in photography, pharmaceuticals, and for the synthesis of amyl derivatives.

Typical Properties and Specifications

Boiling point	130.5°C
Coefficient of expansion	0.00089 per °C
Flash point (Open Cup)	115°F
Heat of vaporization	100.5 cal./g (calc'd.)
Melting point	−117.2°C
Specific gravity at 20/20°C	0.81–0.82
Refractive index at 20°C	1.4099
Specific heat at 75°C	0.686 cal./g
Viscosity at 24°C	3.86 centipoises
59°C	1.48 centipoises
Weight per gallon at 20°C	6.79 lbs.
Acidity (mg KOH per g)	0.06 (max.)
Distillation range	128.0–132.0°C
Residue	0.003 g/100 cc (max.)

Active Amyl Alcohol (2-Methyl-1-Butanol, *sec*-butyl carbinol,) [$CH_3—CH_2—CH(CH_3)—CH_2OH$]. Active amyl alcohol is a water-white primary alcohol. It is slightly soluble in water but miscible with ether, benzene, and naphtha. It finds use in organic syntheses.

Typical Properties and Specifications

Boiling point	128°C
Coefficient of expansion per °C	0.00078
Distillation: 95%	between 125.0–131°C (min.)
30%	above 130°C (max.)
Flash point (Open Cup)	122°F
Heat of vaporization	100.0 cal./g (calc'd.)
Melting point	< −70°C
Specific gravity at 20/4°C	0.816
Refractive index at 20°C	1.4097
Viscosity at 20°C	5.09 centipoises
60°C	1.44 "
Weight per gallon at 20°C	6.80 lbs.
Acidity (mg KOH per g)	0.06 (max.)
Residue	0.003 g/100 cc

tert.-**Amyl Alcohol (Refined).** (2-Methyl-butanol-2, dimethylethyl carbinol) [$(CH_3)_2COH \cdot C_2H_5$]. *Tert.*-amyl alcohol is a water-white, low-boiling liquid. It is only partly soluble in water but is almost completely soluble in methanol, ethyl ether, ethyl acetate, acetone, aromatic and aliphatic hydrocarbons, fixed oils, oleic and hot stearic acids, and hot paraffin and caranauba waxes, the latter two solidifying when cooled. It is useful in nitrocellulose lacquer formulations.

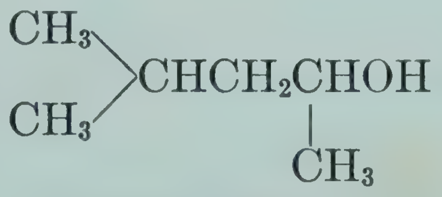
Typical Properties and Specifications

Boiling point	101.8°C
Coefficient of expansion per °C	0.00133 (calc'd)
Flash point (Open Cup)	75°F
Heat of vaporization	93.4 cal./g
Melting point	−11.9°C
Odor	Camphor-like
Specific gravity at 20/4°C	0.809
Refractive index at 20°C	1.4052
Specific heat	0.753 cal./g
Viscosity at 25°C	3.70 centipoises
at 63°C	0.99 "
Water Miscibility	22% by vol. (min.)
Weight per gallon at 20°C	6.75 lbs.
Acidity (as ascetic acid)	0.15% max.
Distillation range	95% between 99.8–103.8°C
Initial boiling point	Not below 99.5°C
Final boiling point	Not above 103.0°C
Nonvolatile matter	0.003 g/100 cc (max.)

HEXANOLS

***n*-Hexanol** [$CH_3(CH_2)_4CH_2OH$]. *n*-Hexanol is a water-white liquid miscible with most organic solvents but only slightly soluble in water. It is used mainly in the manufacture of pharmaceuticals.

Boiling point	157°C
Color	Water-white
Dryness	Miscible with 19 vol. 60° Bé. gasoline at 20°
Flash point	165°F
Solubility in water at 20°C	0.58%
Solubility of water in *n*-hexanol at 20°C	7.2%
Specific gravity at 20/20°C	0.819 to 0.823
Weight per gallon at 20°C	6.83 lbs.
Acidity (as acetic acid)	0.01% max.
Distillation range at 760 mm	153.5°–157.0°C
Nonvolatile matter	0.005 g/100 cc (max.)

Methyl amyl alcohol. 

$$\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right>CHCH_2\underset{\underset{CH_3}{|}}{CHOH}$$

(methyl isobutyl carbinol)

methyl amyl alcohol is a colorless, stable liquid. It is miscible with most of the commonly used organic solvents and is a solvent for oils, fats, waxes, resins, camphor, blown oils, dyes and so forth. It is used as a medium-boiling solvent in lacquer formulation and in the manufacture of xanthates, oil additives and in ore flotation.

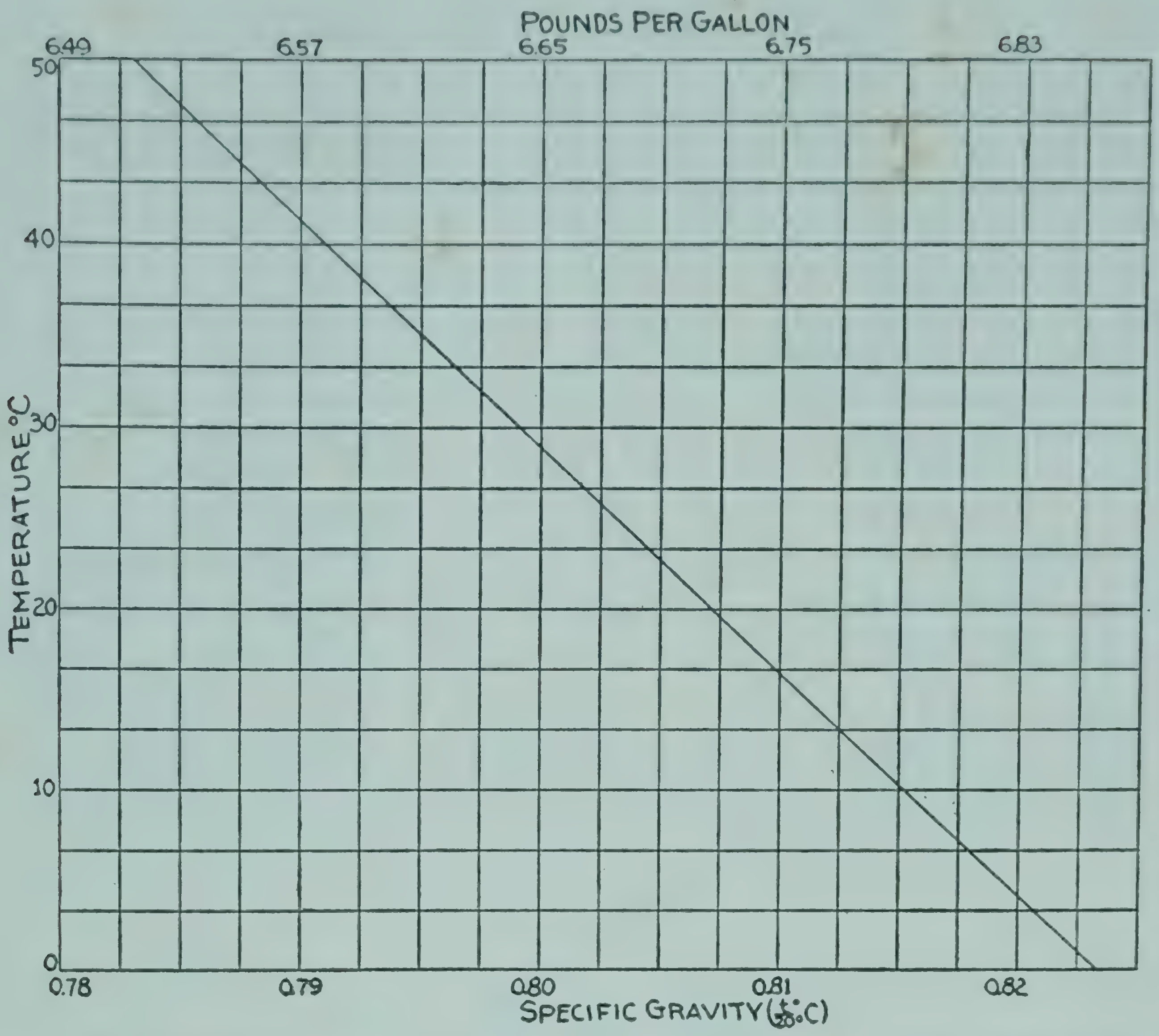


FIGURE 11.46. Specific Gravity and Weight per Gallon of Methyl Amyl Alcohol at Various Temperatures.[3]

The physical properties and solvency characteristics previously discussed in addition to those treated in detail in the following sections will aid manufacturers in using methyl amyl alcohol for the following applications:

1. In nitrocellulose lacquers.
   (a) as a latent solvent.
   (b) as an additive to ketones, such as methyl isobutyl ketone, to modify the evaporation rate and increase blush-resistance.
2. In miscellaneous coating materials.
   (a) Ethyl cellulose
   (b) Alkyds
   (c) Phenolic resins
3. For miscellaneous uses.

The use of methyl lacquer formulation assists in promoting good flow characteristics, leveling and gloss. The evaporation rate (0.3; normal butyl acetate = 1.0) assures good blush resistance and makes this alcohol especially useful in the preparation of brushing and hot-spray lacquers. Even though the boiling point (132°C.—approx.) places it in the class of medium boiling compounds, methyl isobutyl carbinol can be employed

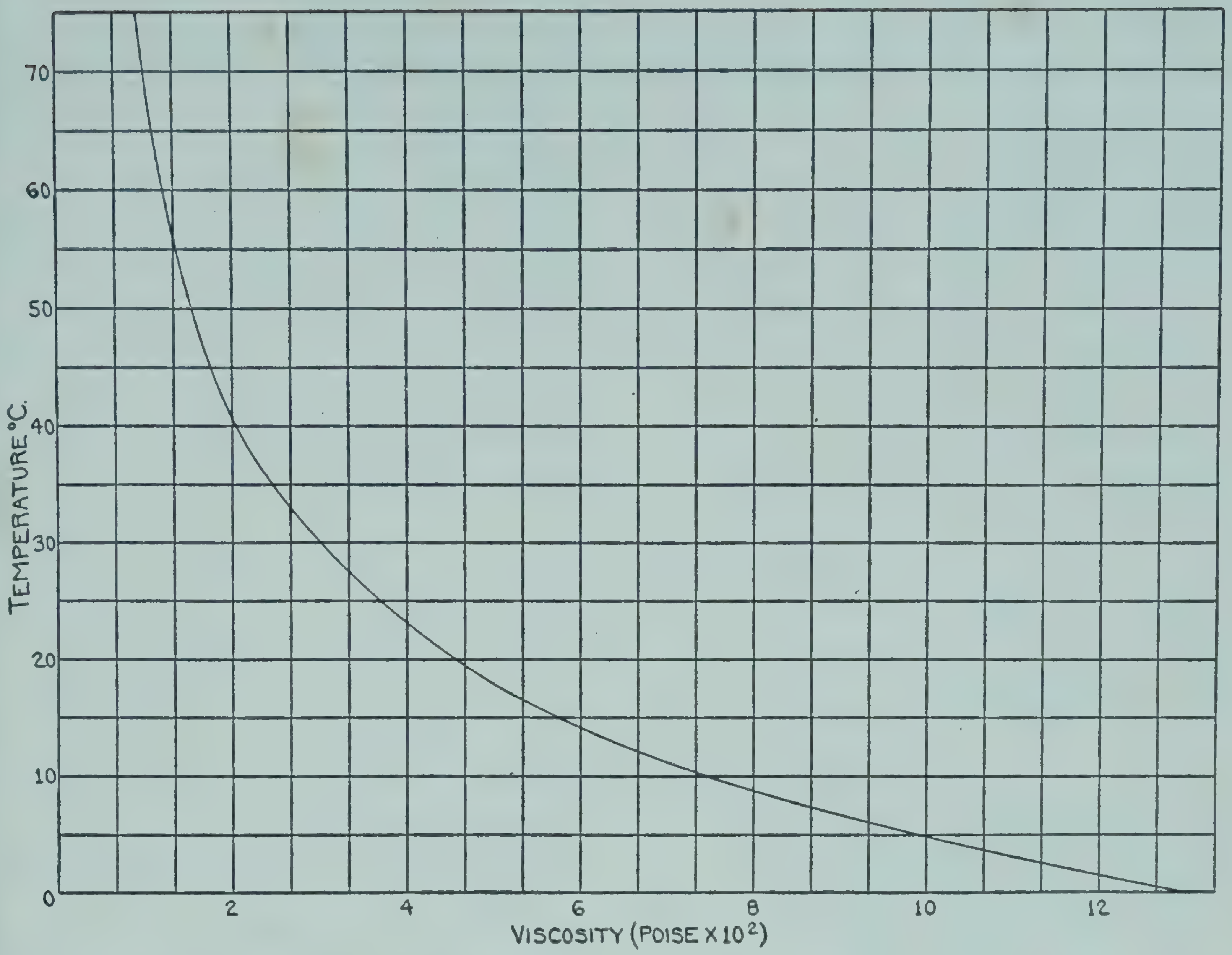


FIGURE 11.47. Viscosity of Methyl Amyl Alcohol at Various Temperatures.[3]

to advantage where some of the primary alcohols of lower boiling point are commonly used. Furthermore, blends of methyl with faster-evaporating alcohols such as ethyl and isopropyl contribute good blush resistance without impairment of solvent release when incorporated in a lacquer formula. Moreover, these blends show excellent latent solvent action for active solvents such as normal butyl acetate or methyl isobutyl ketone without a material change in viscosity.

Methyl isobutyl ketone is used extensively in lacquer formulations as an active solvent for nitrocellulose and various resins. In practice it is sometimes desirable to modify the evaporation rate of methyl isobutyl ketone with higher boiling components so as to increase the blush resistance characteristics. Thus by incorporating limited amounts of methyl amyl alcohol with methyl isobutyl ketone, a blend is produced which has not only higher blush resistance but also increased tolerance for hydrocarbon diluents.

Aromatic diluents with small portions of amyl alcohol are good solvents for ethyl cellulose and synthetic baking-type finishes based on urea-formaldehyde and alkyd resins. The low viscosity of the solutions obtained is due to the presence of alcohol. The moderate evaporation rate of the alcohol furthermore tends to eliminate bubbling during the baking opera-

Table 11.12. Solubility of Various Materials in Methyl Amyl Alcohol[5]

Soluble, over 5% w. concentration

A.D.M.—100 Oil
Castor oil (raw)
Crude Coconut oil
Dammar (dewaxed)
  Batavia
  Borneo
  Singapore No. 2
  Pale Bold East India
  Black East India
Ester gum
Ethyl cellulose (T-100)
Gum elemi
Helix wood rosin (Ind.)
Light rosin (W. G.)
Mineral oil (70/80 Viscosity)
Oleic acid (Tech. Red Oil)
Pine oil
Pure raw linseed oil
Raw cottonseed oil
Soybean oil (2–3 viscosity)
Stearic acid (T.P.)

Soluble, 0.5% w.–5% w. concentration

China wood oil
Gum mastic
Gum Philippine Manila
Gum pontianak
Kauri No. 114 (Brown Kauri)

Soluble, less than 0.5% w. concentration

Air blown asphalt (150° F.M.P.)
Air blown asphalt (170° F.M.P.)
Basic Blue dye No. 623 Conc., P.D.R. 1944 (Krieger)
Blue acetate dye (Sandoz)
Gilsonite pitch
Hard cottonseed pitch (185°/200°F., M.P.)
Oil Special red dye No. 1 (Krieger)
Orange acetate dye
Paving asphalt (Gilmore, 51/60, Penetration)
Red Acetate dye (Sandoz)
Soft Cottonseed Pitch (100°F., M.P.)
Steam Refined Asphalt (10/20, Penetration)
Thermoil A
White Kauri (SO-2, Superior)

Insoluble

Acid Fast Red dye Conc. P.D.R., 301 M. (Krieger)
Alkyd, drying type medium oil
Alkyd, drying type short oil
Alkyd, maleic modified
Alkyd, non-drying type
Beeswax, yellow
Carnauba wax (No. 3 N.C.)
Cellulose acetate (Hercules Grade P.M. 3)
Cellulose triacetate (Hercules T.L. I.)
Congo gum No. 813 (East India Congo)
Congo gum No. A-217—swells
Direct Sky Blue dye Conc. B.B.A. 2995 M. (Krieger)
Formvar "E" (Shawinigan—Polyvinyl formal)
Hercose C. N. (Cellulose Acetate Butyrate)
Lanolin (U.S.P.)
Pale Cracked Congo (Run Congo Gum)—swells
Pale East India Chips (Gum Macassar, Hairo D)
Raw Neoprene
Spermaceti Wax, white (U.S.P.)
Spirit Fast Yellow dye (Krieger)
Styron YA5-K27 (Dow)
Vinyl resin XYHL—swells
Vinyl resin VYHH
Vinyl resin VYNW
Vinyl resin VYLF
Vinyl resin AYAF—swells
Vinyl resin VYNU
Vinyl resin VYHM—swells
Vinyl resin XYNC—swells
Vinyl resin VYNS
Vinyl resin VMCH

tion. Methyl isobutyl carbinol is also useful as a solvent for the phenolic resin type baking finishes since its low water solubility lessens dehydration of the gelatin rolls used in the roller coating application of these finishes.

Other applications of methyl amyl alcohol includes its use in the manufacture of various esters, such as the acetate, sebacate and phthalate, and derivatives such as methyl amyl xanthate used as a collector in ore flotation. Certain physical properties, particularly its low solubility in water and compatibility with cresylic acid and pine oil, make methyl amyl alcohol suitable as a frother for ore flotation.

Typical Properties and Specifications

Boiling point	131.4°C
Surface tension	25.1 dynes/cm. (25°C)
Viscosity	0.0459 poise (20°C)
Vapor pressure	3.52 mm. Hg (20°C)
Specific heat	0.654 cal./g. (25°C)
Latent heat of vaporization	102.0 cal./g. at B.P.
Flash point (A.S.T.M. open cup)	45.6°C (114°F)
Solubility in water	1.73% by wt. (20°C)
Solubility of water in methyl amyl alcohol	6.39% by wt. (20°C)
Electrical conductivity	7×10^{-8} recip. ohm (25°C)
Coefficient of expansion (per °C)	0.001000 to 20°C 0.001038 to 55°C
Refractive index	1.4089 (25°C)
Specific gravity	$0.8072 \frac{20°C}{20°C}$
Weight per gallon	6.72 lb. (20°C)

2-Ethylbutyl Alcohol (2-Ethylbutanol) $[CH_3\cdot CH_2\cdot CH(C_2H_5)\cdot CH_2OH]$. 2-Ethylbutanol was originally known as pseudo hexyl alcohol and was first prepared in 1890. It is a colorless, stable, medium-boiling liquid, very slightly soluble in water, but miscible with most organic solvents. It will dissolve a large variety of oils, gums, natural resins, waxes, dyes, etc., *e.g.*, beeswax, carnauba wax, castor oil, ceresin wax, coumarone, dewaxed dammar, ester gum, ethylcellulose, linseed oil, mineral oil, oil and spirit-soluble nigrosine, oil of pine leaves, rosin, bleached shellac, and tung oil.

It is used as a solvent and diluent in lacquers and synthetic resin varnishes and where a medium-boiling alcohol is desired. It is also used in the manufacture of barbiturates and flavoring materials, plasticizers and other derivatives.

Typical Properties and Specifications

Acidity (as acetic acid)	0.02% max.
Boiling point	148.9°C
Coefficient of expansion per °C	0.000892 to 20°C 0.000921 to 55°C

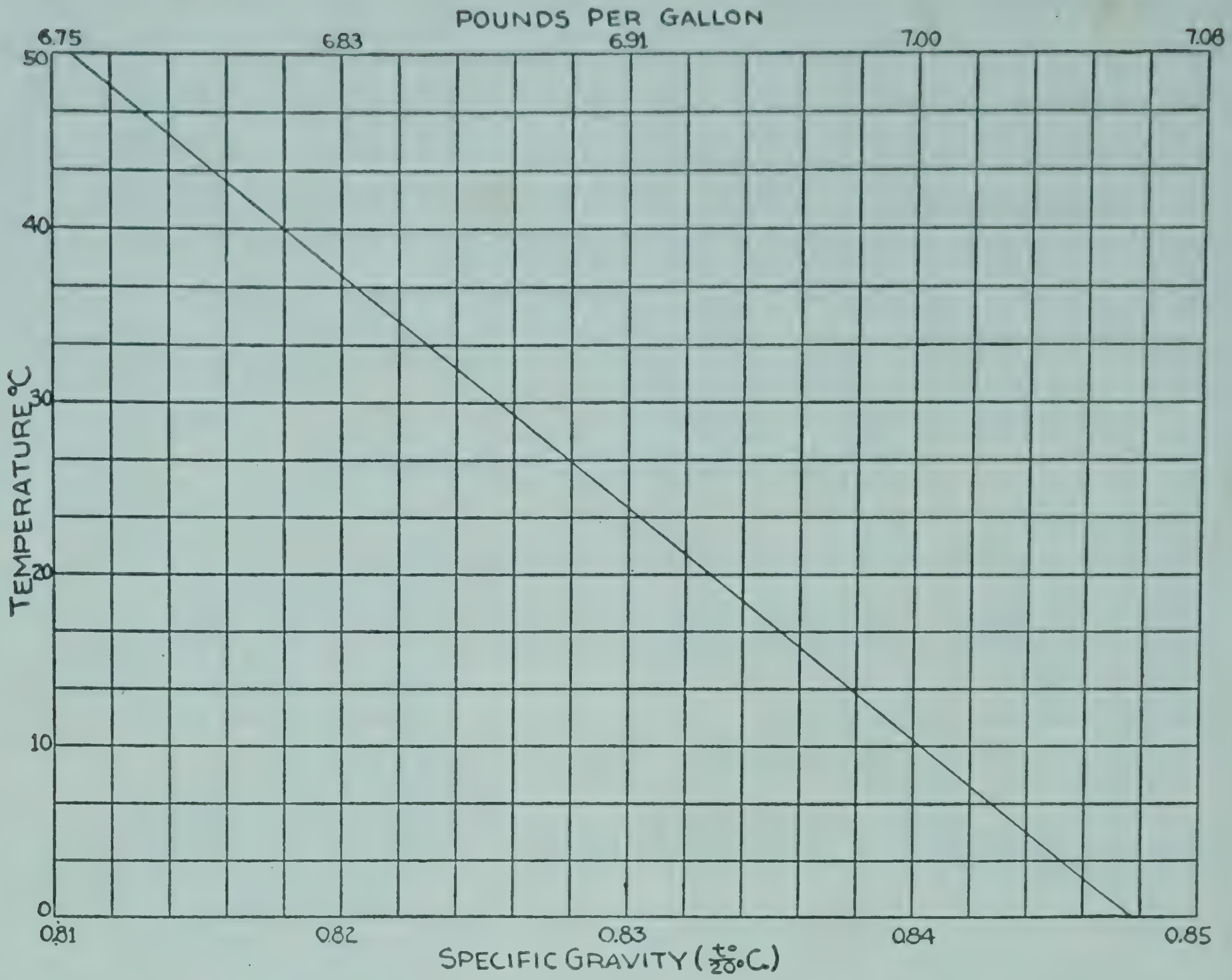


FIGURE 11.48. Specific Gravity and Weight per Gallon of 2-Ethyl Butyl Alcohol at Various Temperatures.[6]

Color		Water-white
Dryness		Miscible with vol. of 60° Bé gasoline at 20°C
Flash point (ASTM Open Cup)		58°C
Latent heat of vaporization at B.P.		108.9 cal./g
Solubility in water at 20°C		0.43% by wt.
Solubility of water in solvent at 20°C		4.56% by wt.
Specific gravity at 20/20°C		0.8328
Refractive index at 20°C		1.4229
Specific heat at 25°C		0.586 cal./g
Surface tension at 28°C		28.05 dynes/cm
Vapor pressure at 20°C		1.80 mm
Viscosity at 20°C		0.0563 poise
Weight per gallon at 20°C		6.93 lbs.
Boiling range at 760 mm:	Below 140°C	None
	Below 145	Not more than 5%
	Below 155	Not less than 95%
	Above 160	None
Non-volatile matter		0.005% max.

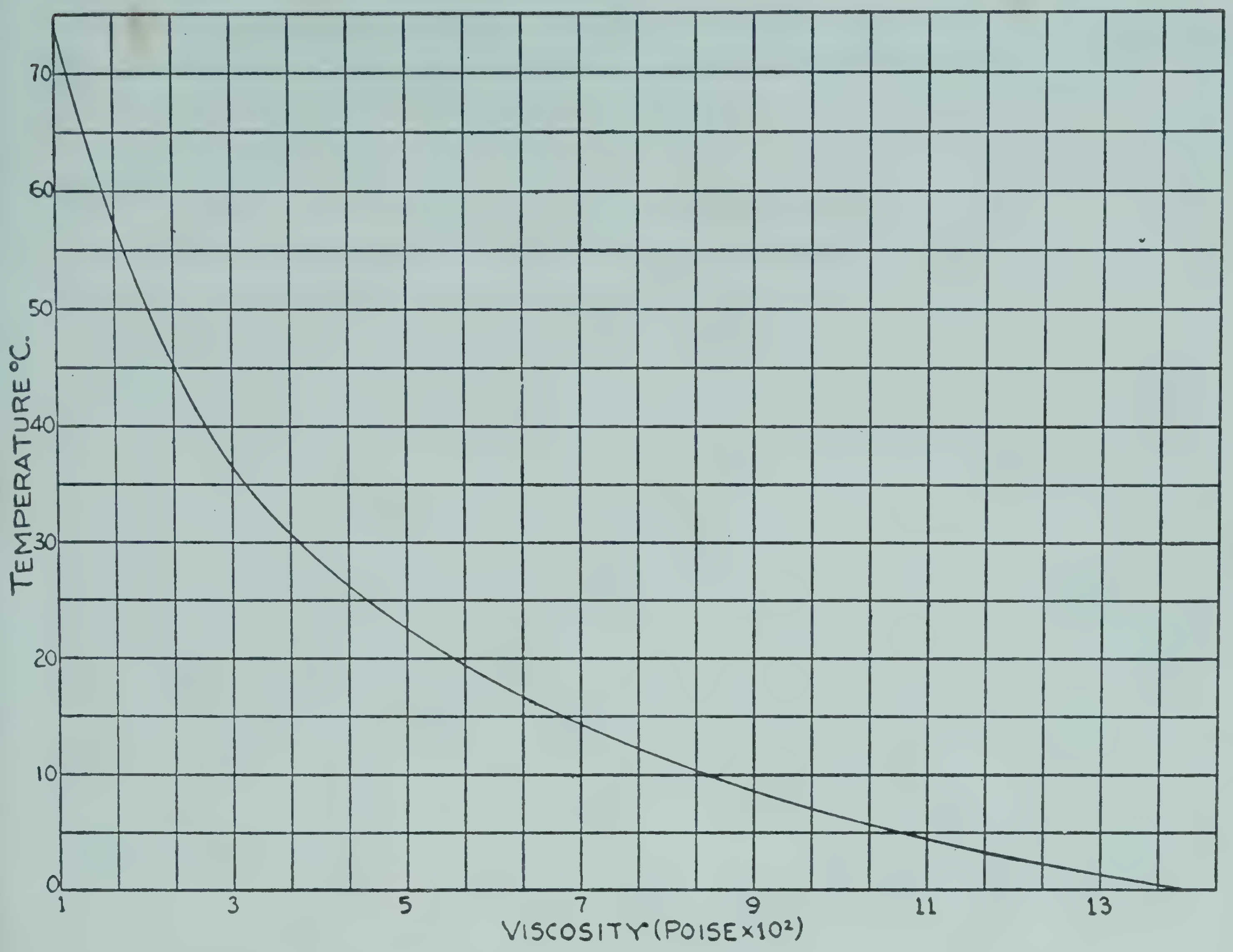


FIGURE 11.49. Viscosity of 2-Ethyl Butyl Alcohol at Various Temperatures.[6]

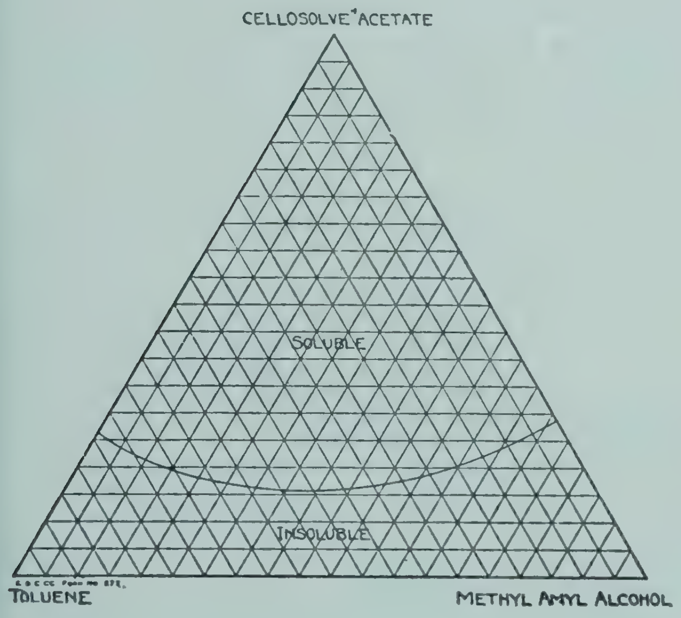


FIGURE 11.50. Solubility of ½-Second R.S. Nitrocellulose in Mixtures of "Cellosolve" Acetate, Toluene, and Methyl Amyl Alcohol.[6]

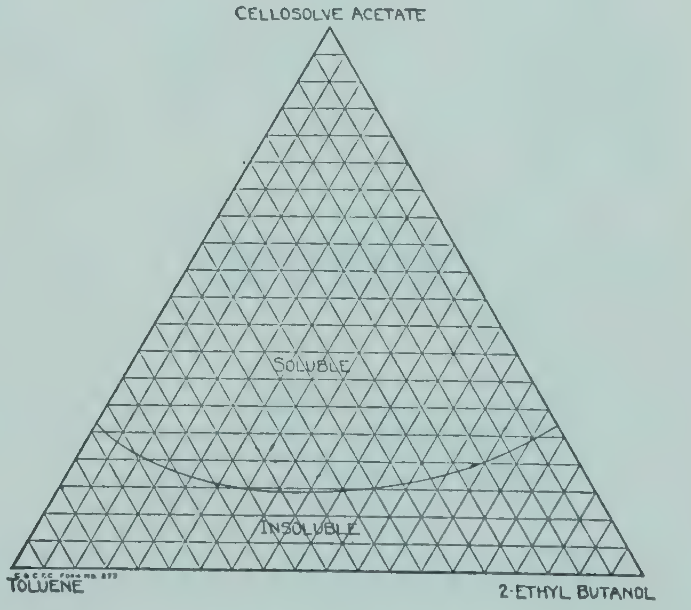


FIGURE 11.51. Solubility of ½-Sec. R.S. Nitrocellulose in Mixtures of "Cellosolve" Acetate, 2-Ethyl Butanol and Toluene.[6]

Heptanol-2 (Methyl amyl carbinol, heptyl alcohol) $[CH_3(CH_2)_4CHOHCH_3]$. This secondary alcohol is the first heptyl alcohol to appear commercially. It is a stable, colorless liquid with a mild odor and miscible with most common organic solvents. Like the higher alcohols it is a solvent for gums, waxes, natural and synthetic resins, animal, vegetable and mineral oils, fats, and dyes. When mixed with other substances it enhances their solvent action; thus it is used in the manufacture of lacquers, where its addition to nitrocellulose solvents causes an increase in their solvency. Its derivatives are used in pharmaceuticals, plasticizers, wetting agents, and in xanthates. Its esters are used in perfume manufacture.

Typical Properties and Specifications

Boiling point at 760 mm	160.4°C
Dryness at 20°C	Miscible with 19 vols. 60° Bé gasoline
Flash point (Open Cup)	160°F
Specific gravity at 20/20°C	0.8160 to 0.8210
Solubility in water at 20°C	0.35% by wt.
Solubility of water in solvent at 20°C	5.80% by wt.
Weight per gallon at 20°C	6.81 lbs.
Acidity (as acetic acid)	0.030% by wt. (max.)
Boiling range at 760 mm: Below 155°C	None
Above 165	None
Below 158	Not more than 5%
Below 162	Not less than 95%
Color	15 (Pt-Co scale) max.

Heptanol-3. Heptanol-3 is an essentially pure compound, with an alcohol content above 99% and a carbonyl content below 1%. The purity of Heptanol-3 is comparable to the commercial grade of other synthetic alcohols.

Alcohol as Heptanol	99% by weight
Carbonyl Compounds	1% " "
Acidity	0.02% by weight
Color	5° APHA (Pt-Co Scale)
Boiling range, 760 mm.	153–158°C
Specific gravity 20/20°C	0.823

The physical properties of the two grades are as follows:

	Heptanol-3	Heptanol Special
Boiling point, 760 mm.	156.2°C	156.7°C
Vapor pressure, 20°C	0.58 mm.	0.90 mm.
Water solubility	slight	slight
Specific gravity, 20/20°C	0.8224	0.8255
Weight per gallon, 20°C	6.84	6.87

For uses such as defoaming, mineral flotation, and general solvent purposes, both materials have possibilities. For uses where the carbonyl content (ketone or aldehyde) of Heptanol Special may be objectionable, such as the preparation of derivatives or as a solvent for materials capable of reacting with the C=O group, Heptanol-3 is more promising.

OCTANOLS

Of the three commercially available 8-carbon atom alcohols 2-ethylhexanol is perhaps the most important. Substantial quantities of these alcohols are utilized in the production of esters of phthalic and sebacic acids, as resin plasticizers. New isomeric octanols derived by the oxo-synthesis, have recently become available.

n-Octanol (Octanol-1, n-Octyl alcohol) [$CH_3(CH_2)_6CH_2OH$]. Commercial n-octanol is derived synthetically from coconut oil. It is used in the manufacture of plasticizers for vinyl resins and other plastics. Other suggested uses for this solvent are as a defoaming agent and in chemical synthesis.

Boiling point	194–195°C
Color	Water-white
Distillation range	90% between 193–196°C
Melting point	−16°C
Solubility in water	0.01%–0.05%
Specific gravity at 25/25°C	0.8225–0.8250

2-Ethylhexanol (2-Ethylhexyl alcohol) [$CH_3CH_2CH_2CH_2CH(C_2H_5)CH_2OH$]. 2-Ethylhexanol, one of the 89 theoretically possible isomeric octyl alcohols, is a colorless, high-boiling liquid, slightly soluble in water but miscible with most organic solvents. It will dissolve a wide variety of vegetable oils and dyes as well as natural and synthetic gums and resins. Its principal use is as a chemical intermediate in the manufacture of plasticizers, wetting agents and the lacquer solvent, 2-ethylhexyl acetate. It is also an excellent defoaming agent and viscosity adjuster in urea formaldehyde coatings.

Physical Properties

Boiling point	184.3 C
Coefficient of expansion per °C	0.000875 to 20°C 0.000902 to 55°C
Flash point (ASTM Open Cup)	71.0°C
Latent heat of vaporization at B.P.	92.8 cal./g
Solubility of water in alcohol at 25°C	2.55% by wt.
Solubility in water at 25°C	0.14% by wt.
Specific gravity at 20/20°C	0.8344
Refractive index at 20°C	1.4300
Specific heat at 25°C	0.564 cal./g
Surface tension at 22°C	30.0 dynes/cm

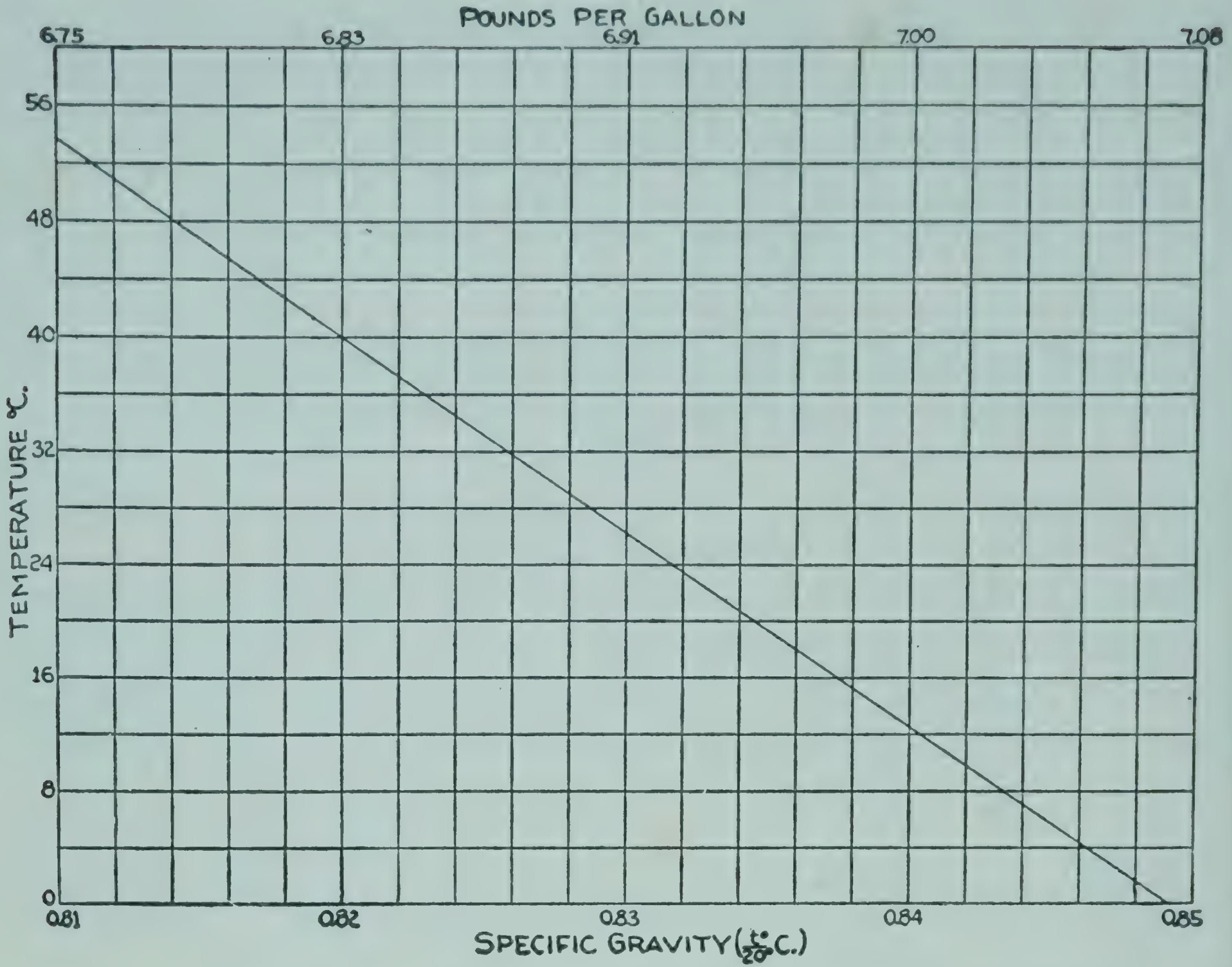


FIGURE 11.52. Specific Gravity and Weight per Gallon of 2-Ethylhexanol at Various Temperatures.[6]

Vapor pressure at 20°C	0.29 mm.
Viscosity at 25°C	0.0707 poise
Weight per gallon at 20°C	6.94 lbs.
Constant-boiling mixture	
2-Ethylhexanol 20% Water 80%	B.P. 99.1°C

Capryl Alcohol (2-Octanol, *sec.*-octyl alcohol) [$CH_3(CH_2)_5CHOHCH_3$]. This secondary octyl alcohol produced commercially by the destructive distillation of castor oil, is a water-white, high-boiling liquid miscible with most organic solvents, including aromatic and aliphatic hydrocarbons and practically insoluble in water. It is used in lacquers and enamels for improved luster and leveling and to promote flow. It also reduces the tendency to sag, since relatively small amounts are used. It is used in long-oil ureaformaldehyde resins, entering into the reaction and acting as solvent and viscosity regulator for the finished resin solution. It is used in alcohol-soluble, heat-hardening phenolic resins where it promotes flow and leveling without pin-holing and cratering. It is an antifoaming agent, and an ingredient of wetting agents used in mercerizing. It is used to some extent in hydraulic brake fluids, and in the manufacture of resin plasticizers.

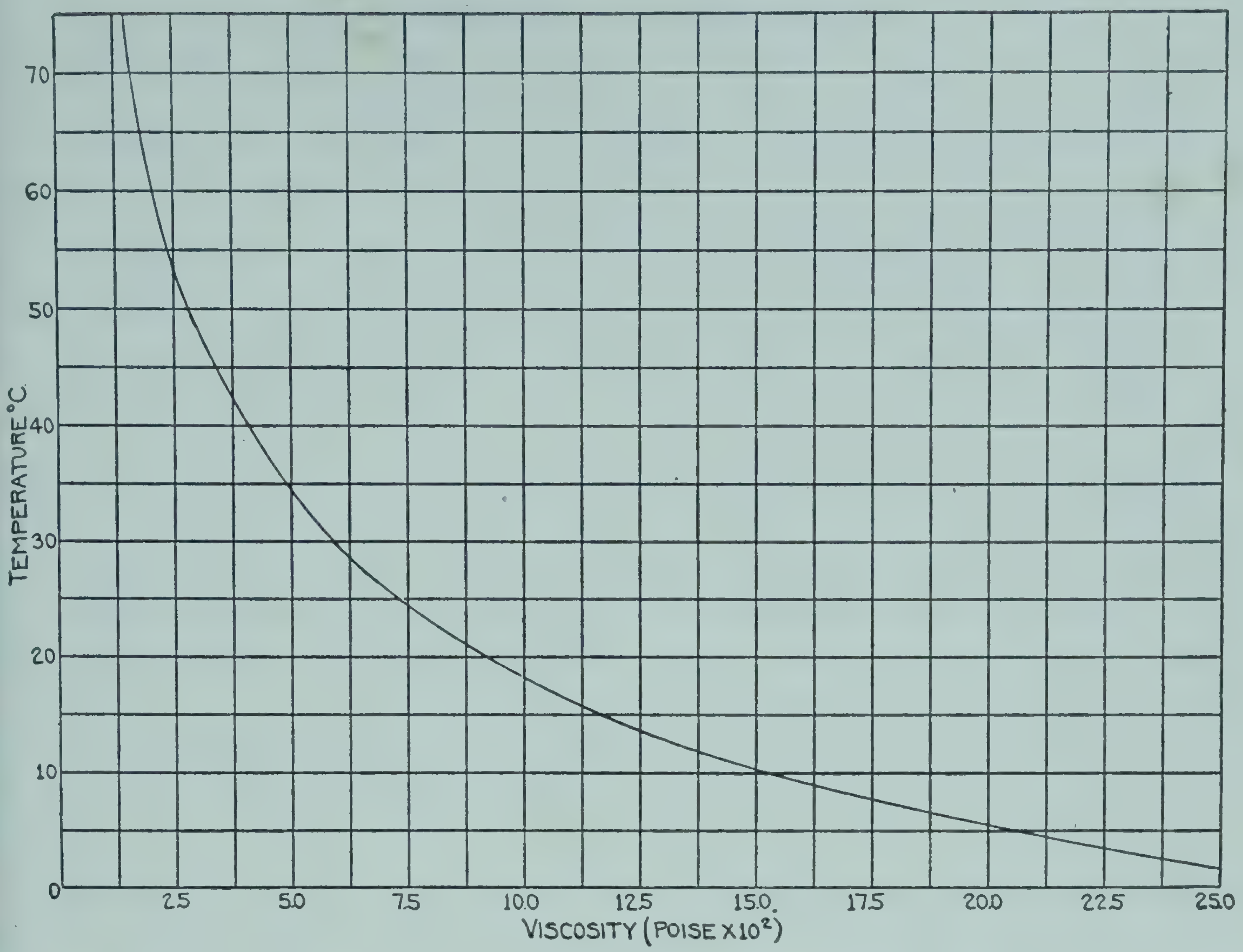
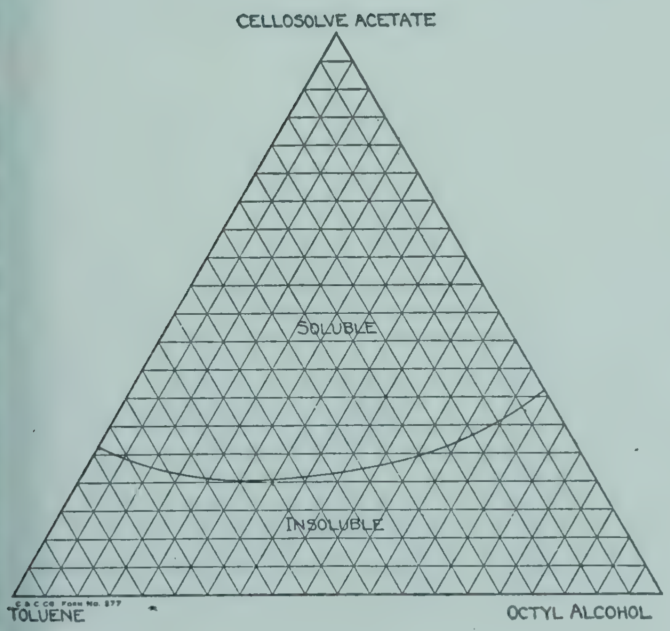


FIGURE 11.53. Viscosity of 2-Ethylhexanol at Various Temperature.[6]



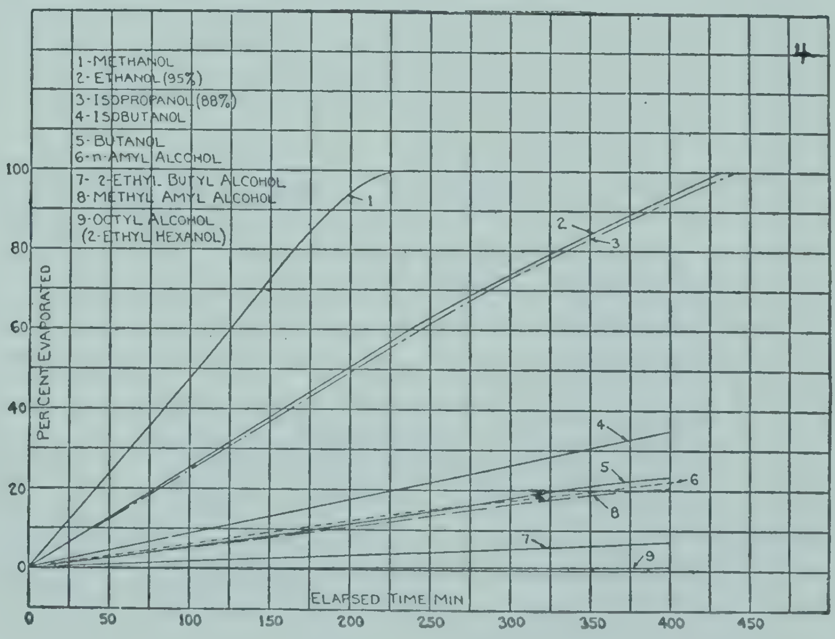


FIGURE 11.54.
Solubility of ½-Sec. R. S. Nitrocellulose in Mixtures of "Cellosolve" Acetate, 2-Ethyl-hexanol and Toluene.[6]

FIGURE 11.55.
Evaporation Rate of Various Alcohols at Room Temperature.[6]

Typical Properties and Specifications

	Solvent Grade	Refined Grade	Chemical Grade
Color	Water-white and clear		
Distillation range	170–177°C	173–178°C	173–180°C
Flash point (°F)	150	165	180
Solubility in water at 20°C	Less than 0.1%		
Specific gravity at 20/20°C	0.8241	0.8206	0.8232
Weight per gallon at 20°C	6.87 lbs.	6.84 lbs.	6.86 lbs.
Boiling range	90% between 174° and 180°C		
Methyl hexyl ketone content	14% max.	8.0% max.	2.0% max.

Nonyl Alcohol. Commerically available for the first time in 1949, nonyl alcohol is a mixture of branched chain primary alcohols. The general formula is RCH_2OH where R is a branched octyl radical. The branching is of a simple character, the principal component being trimethylhexanols, with dimethyl-heptanols as a minor component. These isomers boil in a narrow range as shown below.

Distillation of nonyl alcohol in the presence of water gives an azeotrope boiling at 98–99°C. and containing approximately 15 volume percent of nonyl alcohol.

Potential direct uses of nonyl alcohol are principally in the formulation of lacquers and enamels, as a dispersing and wetting agent either alone or as a modifier for other wetting agents, as a component of penetrating oils, and as a defoaming agent.

As an intermediate in the production of medium and high-boiling esters and a wide variety of other derivatives, it offers possibilities in many fields. Condensation of ethylene oxide with nonyl alcohol, or with its derivatives such as nonyl mercaptan, likewise presents a variety of products potentially useful as surface-active agents, etc.

Typical Properties

Aldehyde Content	0.30 wt. %
Neutralization Number	0.02 mg KOH/g
Color, Saybolt	30
Mixed Aniline Point	−15°C
Solubility in H_2O (25°C)	<0.05 wt. %
Viscosity	
130°F	8.0 centistokes
100°F	10.4 "
−40°F	633 "
Flash point (open cup)	80°C
ASTM Distillation—Initial	193°C
5%	196°C
50%	198°C
95%	201°C
Max.	206°C

Temp. at 50% point	
5 mm pressure	78°C
100 mm "	138°C
760 mm "	198°C
Heat of vaporization (Lv)	
100°F	22,000 BTU/lb mol
300°F	19,000 "
400°F	17,400 "
Refractive Index	1.4390 N_D^{20}
Specific Gravity	0.845 (15.6°/15.6°C)

Nonyl Alcohol Derivatives. Nonyl alcohol enters readily into the reactions characteristic of primary alcohols. There is no significant difference in the chemical reactivity of the various isomers. This is exemplified by the fact that a wide variety of derivatives are obtained in high yields under relatively mild reaction conditions.

The derivatives described in the following pages have been prepared on a small scale only, but the properties shown are believed to be typical. Procedures employed were conventional and in most cases would be adaptable to commercial scale operations.

The physical properties of typical nonyl esters are summarized in Table 11:13. These derivatives have been made conventionally by heating the acid and the alcohol, in the presence of a trace of an acidic catalyst, the water of reaction being removed as an azeotrope with a solvent such as toluene or xylene. The carbonate can be made by condensing the alcohol with phosgene

Diisobutyl Carbinol.* Diisobutyl carbinol is a relatively high-boiling, water-white alcohol. It is only slightly soluble in water, but is miscible

TABLE 11.13. ESTERS OF NONYL ALCOHOL

COMPOUND	BOILING POINT,°C	DENSITY (25°C)	REFRACTIVE INDEX N_D^{20}	VISCOSITY IN CENTISTOKES		
				−40°F	100°F	210°F
Nonyl acetate	87– 92 (10 mm)	0.873	1.4260	—	1.77	0.88
Nonyl acrylate	68– 73 (1 mm)	0.884	1.4404	—	—	—
Nonyl methacrylate	76– 78 (1 mm)	0.880	1.4422	—	—	—
Nonyl nonanoate	148–166 (10 mm)	0.863	1.4419	—	—	—
Nonyl benzoate	140–145 (5 mm)	0.961	1.4911	—	5.35	1.68
Dinonyl carbonate	135–140 (0.3 mm)	0.894	1.4427	—	—	—
Dinonyl maleate	157–167 (0.1 mm)	0.941	1.4586	6,900	17.47	3.50
Dinonyl phthalate	205–220 (1 mm)	0.979	1.4871	500,000	55.3	6.3
Trinonyl phosphate	210–230 (1 mm)	0.921	1.4496	7,900	19.0	4.24
Dinonyl adipate	201–210 (1 mm)	0.926	1.4523	3,000	14.9	3.65
Dinonylyldiethyleneglycol bis carbonate	—	1.01	1.4517	—	—	—

---

* Carbide and Carbon Chemicals Corporation.

with most organic liquids. Diisobutyl carbinol and water form a heterogeneous constant-boiling mixture, which contains 29.6% by weight of the alcohol and boils at 98.5°C.

The high boiling point of diisobutyl carbinol indicates value as a solvent and component of urea and melamine-based resins, and as a coupler in conjunction with other active solvents, or diluents, in phenolic and alkyd resin enamels and varnishes, and nitrocellulose inks and brushing lacquers. Esters of diisobutyl carbinol and monobasic acids are suggested as lacquer solvents and perfume ingredients. Its dicarboxylic acid esters are interesting as plasticizers having low volatility.

Diisobutyl carbinol is suggested as a frother in hydrometallurgical processing, and its xanthates should prove interesting as mineral collectors.

Surface-active agents having outstanding properties have been prepared from diisobutyl carbinol. The solubility of water in diisobutyl carbinol is greater than the solubility of the alcohol in water. This indicates that small proportions of diisobutyl carbinol are effective in coupling water into homogeneous phase mixtures with oils and other water-insoluble materials. These mixtures are frequently desirable for high speed cutting oils and textile auxiliaries.

Physical Properties

Boiling point at 760 mm	173.3°C
Vapor pressure at 20°C	0.3 mm. Hg
Freezing point	−65°C
Solubility in water at 20°C	0.06% by wt.
Solubility of water in, 20°C	0.99% by wt.
Specific gravity at 20/20°C	0.8121
Absolute Viscosity at 0°C	56.0 cps.
Absolute viscosity at 20°C	14.3 cps.
Average weight at 20°C	6.75 lb. per gal.

n-**Decanol** (Decanol-1, *n*-Decyl alcohol) [$CH_3(CH_2)_8CH_2OH$]. Primary *n*-decanol is at present the only ten-carbon atom alcohol available in commercial quantities. It has a bland odor and it may be used as a defoaming agent, and as an intermediate in chemical synthesis.

Boiling point	231°C
Color	Color-white
Distillation range (ASTM method)	90% between 228–233°C
Melting point	7°C
Solubility in water	0.01%–0.05%
Specific gravity at 25/25°C	0.8300–0.8380

Undecanol (5-Ethylnonanol-2) [$C_4H_9CH(C_2H_5)C_2H_4CH(OH)CH_3$]. This secondary alcohol is a synthetic branched-chain alcohol that can be compared in molecular size to the fatty alcohols derived from natural vegetable and animal fats and waxes. It is a stable liquid with a mild odor, oxidizing with difficulty and therefore will not turn rancid as a result of polymerization or oxidation. It is used as an antifoaming agent, particularly under high temperatures. It is useful as an intermediate for the manufacture of plasticizers, perfumes, esters, cosmetic bases, pharmaceuticals, wetting agents, detergents, flotation agents, and insecticides.

Boiling point .... 225.4°C

Trimethylnonyl Alcohol (2,6,8-Trimethylnonanol-4) [$(Ch_3)_2CHCH_2 \cdot CHOHCH_2CH(CH_3)CH_2CH(CH_3)_2$]. Trimethylnonyl alcohol is a mild-odored, high-boiling, colorless liquid. This synthetic twelve carbon alcohol is produced as a high purity chemical and is offered at reasonable prices calculated to stimulate industrial uses.

For several years dodecyl mercaptan made from coconut oil has been used as a polymerization aid in synthetic rubber production to prevent premature crosslinking, and improve processing characteristics of GR-S stocks. It is expected that the mercaptan made from trimethylnonyl alcohol will perform this same function with improved economy and manufacturers of dodecyl mercaptan are invited to experiment with this new twelve carbon atom alcohol.

Surface active agent manufacturers will find trimethylnonyl alcohol a valuable new intermediate for experimental and plant scale manufacture of detergent and wetting agent compositions of various types. For example the trimethylnonyl group may be used to alkylate aryl groups which will sulfonate; or trimethylnonyl polyglycol could be prepared. Either type of material would show surface activity in aqueous systems.

For some time 2-ethyl hexanol and other faintly soluble alcohols and higher ethers have been used in a variety of applications where the control of foam is necessary. It is expected that trimethylnonyl alcohol will be an efficient foam breaker for such aqueous systems, and it is quite possible that it will perform even more efficiently than the materials used heretofore.

Special purpose plasticizers may be derived from trimethylnonyl alcohol through esterification with various organic or inorganic acids. The value of these compounds is relatively unexplored and may prove to be a fertile field for investigation.

Boiling point at 760 mm	225.2°C
Freezing point	Sets to a glass below −60°C
Vapor pressure at 20°C	0.01 mm
Solubility in water at 20°C	<0.02% by wt.
Solubility of water in at 20°C	0.6% by wt.
Flash point (Open Cup)	200°F
Specific gravity at 20/20°C	0.8193
Weight per gallon at 20°C	6.83 lb.

Tetradecanol (Tetradecyl alcohol, 7-Ethyl-2-Methylundecanol-4) [$C_4H_9CH(C_2H_5)C_2H_4CH(OH)CH_2CH(CH_3)_2$]. One of the same group in which undecanol and heptadecanol belong. It is a stable liquid with a mild odor and its uses are similar to those of undecanol and heptadecanol.

Boiling point	263.2°C

Heptadecanol (3,9-Diethyltridecanol-6) [$C_4H_9CH(C_2H_5)C_2H_4CH(OH)\cdot C_2H_4CH(C_2H_5)_2$]. Heptadecanol is one of the same group containing undecanol and tetradecanol, and has similar uses. It is a stable liquid with a mild odor; it oxidizes with difficulty, and thus will not turn rancid through oxidation or polymerization.

Boiling point	308.5°C

Phenol (Carbolic acid, C_6H_5OH). Phenol is a colorless, water-soluble crystalline solid having a characteristic odor. When warmed, phenol melts to a clear, colorless liquid. It is soluble in the more commonly known alcohols, aliphatic and aromatic hydrocarbons, chlorinated aliphatic and aromatic hydrocarbons, esters, and ethers; at 67°C it is completely miscible with fixed and volatile oils. Its use is largely limited by its toxic properties. This is also true of the cresols and cresosote oils despite their excellent solvent powers. Phenol is used in the petroleum industry for refining lubricating oils, and is a solutive extractant for the undesirable naphthenic fractions. It is a widely utilized industrial chemical, as indicated by the table of wartime uses. Predominantly used as an ingredient of plastics.

Typical Properties and Specifications

Boiling point		181.6°C
Solidifying point		Not less than 40.7°C
Freezing point		Not less than 40°C
Odor		Characteristic
Solubility in water	Above 68°C	In all proportions
	at 20°C	8.3%
Specific gravity at 41/4°C		1.058
Distillation range		95% distills within a range of 1.5°C
Purity		98%, min.

(Thousands of pounds)*

Use	*Amount*	*Per cent*
Total Allocations	205,186	100.0
Direct military[1]	20,702	10.1
Foreign	23,307	11.3
Other uses	161,177	78.6
Phenolic resins	106,655	52.0
Chemical manufacture[2]	11,806	5.7
Salicylates	11,264	5.6
Petroleum refining[3]	10,857	5.2
Disinfectants and insecticides[4]	5,707	2.8
Triphenyl phosphate and other plasticizers	4,585	2.2
Toluene extraction	4,262	2.1
Dyes and inks	2,187	1.1
Medicinals, other than salicylates	1,733	0.8
Miscellaneous uses and small orders	2,121	1.1

[1] End-use data not available.
[2] Includes substituted phenols.
[3] Includes phenol used in oil additives and oil refining materials.
[4] Includes chlorinated phenols.

Benzyl Alcohol (phenylcarbinol, $C_6H_5CH_2OH$) is a colorless, high-boiling liquid of faint odor. It is miscible with most cellulose ether solvents, aromatic hydrocarbons and oils, and will dissolve such substances as methyl, ethyl, and benzylcellulose, nitro- and acetylcellulose, benzyl abietate and various esters. It is used as a plasticizer; in the manufacture of perfumes, pharmaceuticals, and dyestuffs.

Color	water-white
Flash point	96°C
Fire point	96°C
Freezing point	−15.3°C
Sp. gr. 15.5°/15.5°C	1.047
Refractive index (20°C)	1.539
Boiling range	204–208°C
Acidity	0.1% max.

Cyclohexanol. (Hexahydrophenol, hexalin, anol, hydrophenol, hydralin, adronal, cyclohexyl alcohol) $(\underbracket{CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CHOH})$. Cyclohexanol is a water-white, hygroscopic, slightly toxic liquid with a menthol-like odor. It is a cyclic secondary alcohol made by the catalytic hydrogenation of phenol. It contains, as impurities, hydrogenated phenol- and cyclohexanone. It is miscible with most aliphatic, aromatic, hydrogenated and chlorinated solvents and is a solvent for alkyd resins, benzyl

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* "Facts for Industry," U. S. Bureau of Census, 1944.

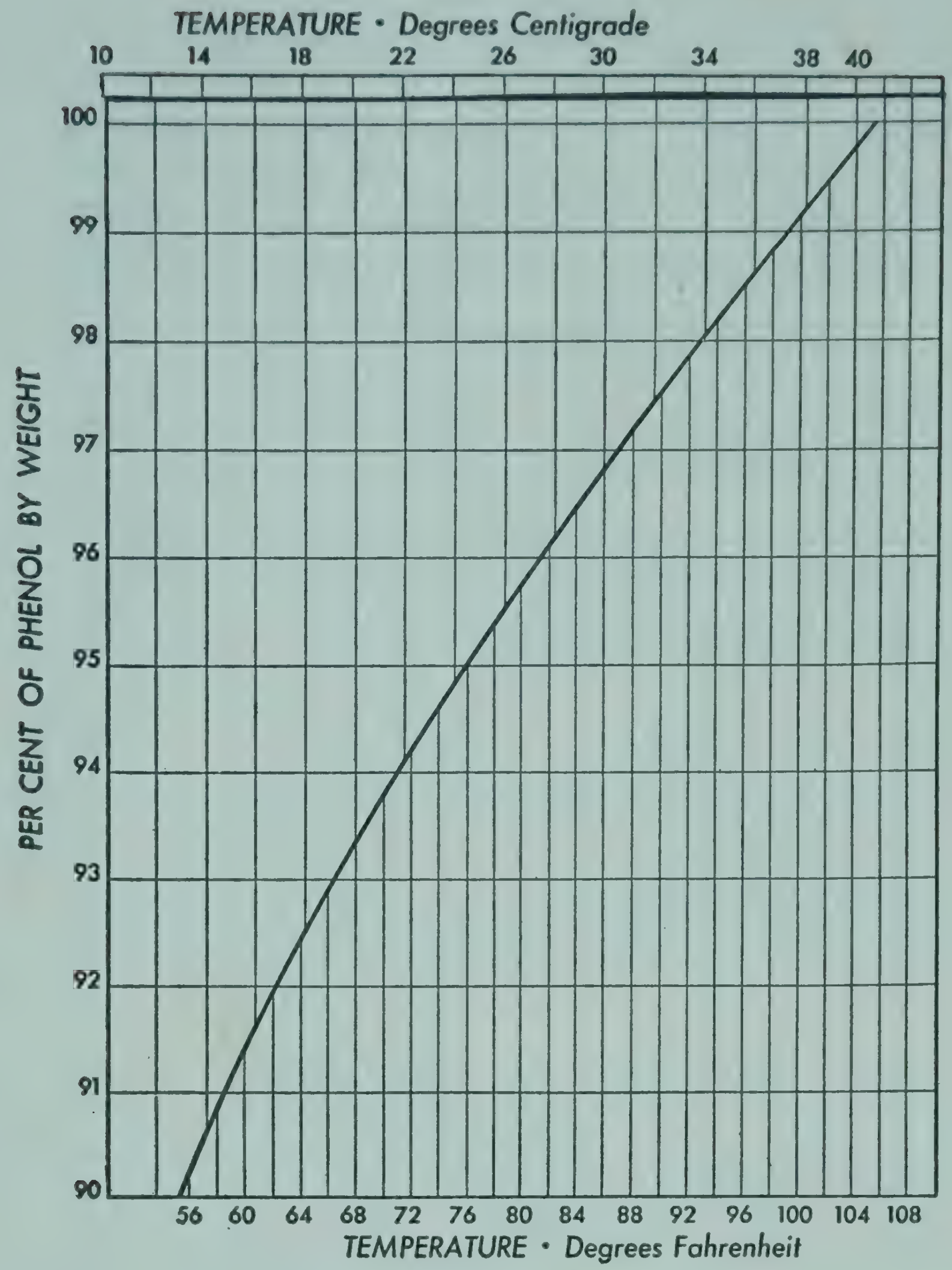


FIGURE 11.56. Freezing Points of Phenol-Water Mixtures.

abietate, coumarone resins, ester gum, kauri, manila, mastic, shellac, metallic soaps, rubber, basic chrome and acid dyes, and essential, mineral and vegetable oils. It will also dissolve some types of cellulose esters and ethers. It will not dissolve cellulose nitrate or acetate. Since cyclohexanol is a powerful mutual solvent, it has the faculty of converting cloudy dispersions into clear solutions.

The presence of cyclohexanol in a solvent mixture will increase the dilution tolerance for coal-tar and petroleum hydrocarbons. Both its solvency and its low volatility promote good primary and also secondary flow, as well as homogeneity throughout all stages of drying, thus producing flat glossy films. By adding this solvent to a xylene solution of alkyd resins the viscosity is reduced, skinning is prevented, and the lead driers are held in solution. It is also added to soaps and detergents to increase their effectiveness in textile processes. It can be made water-soluble by mixing with sulfated higher fatty alcohols, soaps or sulfonated oils and its presence in these solutions will permit mixing with hydrocarbons. When mixed with soap it can be diluted with either water or common solvents indefinitely without precipitation.

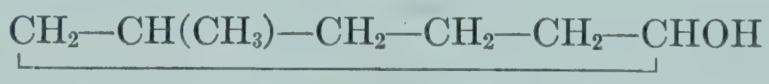
Because of its stabilizing and homogenizing properties for emulsions and other solutions this solvent is used in dry-cleaning, textile cleaning, laundry and household preparations. Other uses for it are in the making of asphalt emulsions, cutting oils, disinfectant emulsions, degreasing leather, wax creams, and polishes. Cyclohexanol also finds use in the preparation of solvent dispersions, emulsifying and dispersing agents for oils, fats, waxes, asphalt, hydrocarbons, dyes, and in printing and dyeing processing, where its solvency and penetrating power are utilized.

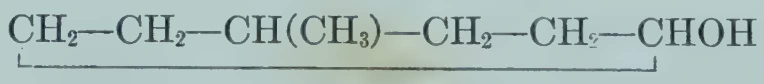
Its excellent blending qualities and low rate of evaporation make it particularly suitable for mixing nitrocellulose with resins and drying oils. When cyclohexanol is present in leather lacquers and dopes it imparts penetrating, plasticizing and softening qualities. Cyclohexanol is used in protective coatings, spirit varnishes, polishes, in paint and varnish removers, as a rayon spotting agent, in perfumes, rubber cements and plasticizer manufacture. It forms constant-boiling mixtures with a number of substances, such as cymene, furfural, xylene, etc.

Typical Properties and Specifications

Boiling point	160.7°C
Color	Water-white
Dielectric constant at 25°C	15.0
Evaporation rate at 45°C (Toluene = 100)	8 (approximate)
Flash point (closed cup)	63°C
Freezing point	15–20°C
Latent heat of Vaporization at B.P.	108 cal./g.
Refractive index at 25°C	1.463–1.465
Solubility in water at 20°C	5.7% (approx.)
Solubility of water in solvent at 11°C	11.3%
Specific heat at 15–18°C	0.417 cal./g.
Viscosity (S.U.V. at 100°F)	81
Water content	Less than 0.2% by wt
Weight per gallon at 20°C	7.9 lbs.
Boiling range	152–162°C
Distillation range	158.0°C–162.0°C 95% distills within 1.0°C
Phenol test	Negative
Purity	98–100%
Residue on evaporation	None

Methylcyclohexanol. (Methyl hexalin, heptalin, hexahydromethyl phenol, hexahydrocresol, sectol, methyl adronol, methyl anol)


$CH_2—CH(CH_3)—CH_2—CH_2—CH_2—CHOH$


$CH_2—CH_2—CH(CH_3)—CH_2—CH_2—CHOH$

Methylcyclohexanol is a colorless, viscous liquid with an aromatic menthol-like odor. The commercial product is a mixture of two cyclic secondary alcohols made by the hydrogenation of meta- and paracresols. Its physical properties are very similar to those of cyclohexanol with the exception of a wider boiling range, owing to the relative amounts of ortho, meta and para compounds. Like cyclohexanol it is a solvent for gums, oils, resins and waxes. It will not dissolve cellulose nitrate or acetate. Its dissolving power is somewhat inferior to that of cyclohexanol, but for all practical purposes, these two solvents can be used interchangeably where evaporation rate is not important.

Typical Properties and Specifications

Boiling point	173.0–175.3°C
Color	Water-white
Evaporation rate approximate (Toluene = 100)	4
Flash point (closed cup)	68°C
Freezing point	−50°C
Refractive index at 25°C	1.456–1.460
Solubility in water at 20°C (approximate)	3–4%
Specific gravity at 25/4°C	0.911–0.916
Viscosity (S.U.V. at 100°F)	76
Weight per gallon at 20°C	7.6 lbs.
Cresol test	Negative
Residue	None
Water content	0.2% max.

Trimethylcyclohexanol

$$[\underbracket{\mathrm{CH(CH_3)\cdot CH_2\cdot CH(CH_3)\cdot CH_2\cdot CH(CH_3)\cdot CH}}\mathrm{OH}].$$

This cyclic primary alcohol is a solid compound. It is soluble in most organic solvents, oils and hydrocarbons, but almost insoluble in water. Some of the suggested uses for this higher alcohol is as a mutual solvent and coupling agent, as an antifoaming agent in hydraulic fluids and textile soaps, in the making of plasticizers, wetting agents, and xanthates.

Boiling point	198°C
Description	solid
Melting point	35.7°C

4-*tert* Amyl Cyclohexyl Alcohol ($C_5H_{11}C_6H_{10}OH$). This is a water-white liquid with an ethereal odor. It is miscible with organic solvents, fixed oils, aromatic and aliphatic hydrocarbons, and oleic acid. It is insoluble in water, and while soluble in hot stearic acid and paraffin and carnauba waxes, these solidify on cooling.

Boiling range	243–249°C
Flash point	212°F
Specific gravity at 20/20°C	0.919

4-*tert*-Amyl Cyclohexyl Alcohol. This is a high-boiling colorless liquid with a mild odor. It is soluble in ethyl ether and naphtha but insoluble in water. It is useful as a chemical intermediate in making plasticizers.

Distillation range	243–249°C
Flash point	212°F
Refractive index at 20°C	1.4765
Specific gravity at 20°C	0.919
Weight per gallon at 20°C	7.7 lbs.

Dimethyl Tolyl Carbinol (Technical) [$CH_3 \cdot C_6H_4 \cdot C(OH)(CH_3)_2$]. This compound is made synthetically from paracymene and contains methyl acetophenone to an extent of 18 per cent or more. The odor of this solvent is like sweet clover. A tertiary alcohol, it resembles pine oil in its solvent and wetting power and is used as a mild disinfectant, as well as in organic synthesis. It decomposes on distillation at atmospheric pressure.

Boiling point at 7 mm	About 100°C
Purity	Technical grade contains from 75 to 85% tertiary alcohol
Specific gravity at 15.5/4°C	0.9823
Refractive index at 20°C	1.5200

Furfuryl Alcohol (alpha-furyl carbinol) ($C_4H_3O \cdot CH_2OH$). Furfuryl alcohol is a yellow to dark amber liquid with an odor suggesting brine. It is miscible with most organic solvents but is immiscible with petroleum hydrocarbons and most oils. It is a solvent for a wide range of organic products such as cellulose ethers and esters, ester gum, coumarone resins and many natural resins. It is a solvent for dyes in textile printing, staining wood, and in abrasives, and is a solvent in phenolic and other types of synthetic resin coatings.

Boiling point	167–177°C (95%)
Flash point (open cup)	75°C
Freezing point	−20°C
Specific gravity at 25/25°C	1.130
Refractive index at 25/D	1.4868
Surface tension	38.2 dynes/cm
Vapor pressure at 30°C	2 mm

Tetrahydrofurfuryl Alcohol (tetrahydrofuryl carbinol) (C_4H_7O—CH_2OH). This alcohol is a water-white to pale yellow mobile liquid with a mild and pleasant odor and stable to light, air, dilute acids and alkalies. Tetrahydrofurfuryl alcohol is miscible with many alcohols, ethers, and will mix with some oils, such as linseed oil and brown soya oil, water, and

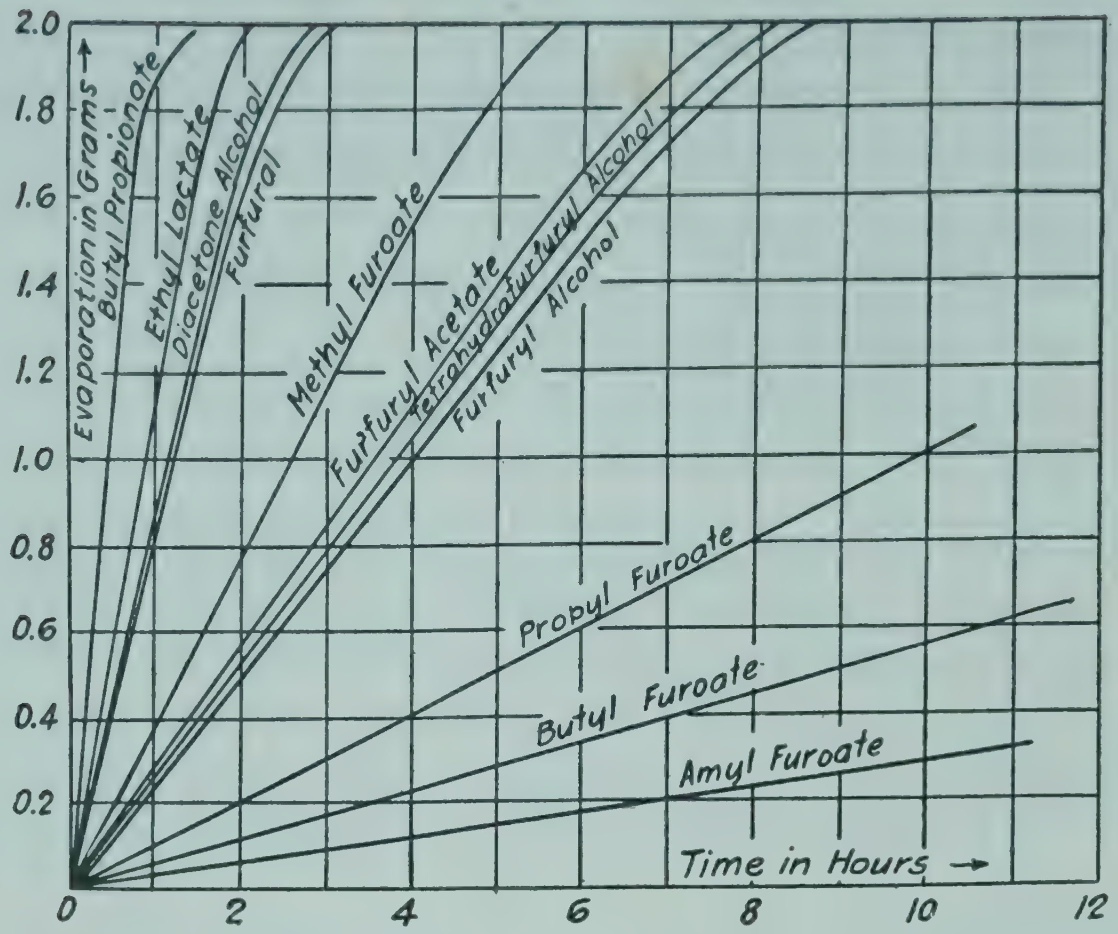


FIGURE 11.57. Evaporation Rate of Furfural and its Derivatives at Room Temperature.[6]

many organic solvents. It is also a solvent or dispersing agent for benzyl cellulose, nitrocellulose, chlorinated rubber, shellac, resin, vinyl and alkyd resins. It is utilized as a solvent in textile dyeing, as a textile wetting and cleaning agent, as a brake fluid diluent and as a stabilizer in gelatin solutions.

Boiling point	170–180°C (99%)
Flash point (open cup)	75–80°C
Specific gravity at 20°C	1.055
Refractive index at 25/D	1.4502
Surface tension	36.5 dynes/cm
Vapor pressure at 50°C	3 mm
at 75°C	16 mm
Viscosity at 25°C	5.49 centipoises
Weight per gallon at 20°C	8.0 lbs.

GLYCOLS

This class of compounds owes its value to the presence of two hydroxyl groups. Thus, when compared with the corresponding monohdyroxyl compounds, they are more hygroscopic, have considerably higher boiling points and lower evaporation rates, and freezing points[7, 12]. In general their properties are intermediate between those of the alcohols and glycerol. These useful properties make the glycols particularly suitable as antifreeze agents[8] and as softening agents in casein and hide glues, in paper, textiles, and moulded compositions.[9]

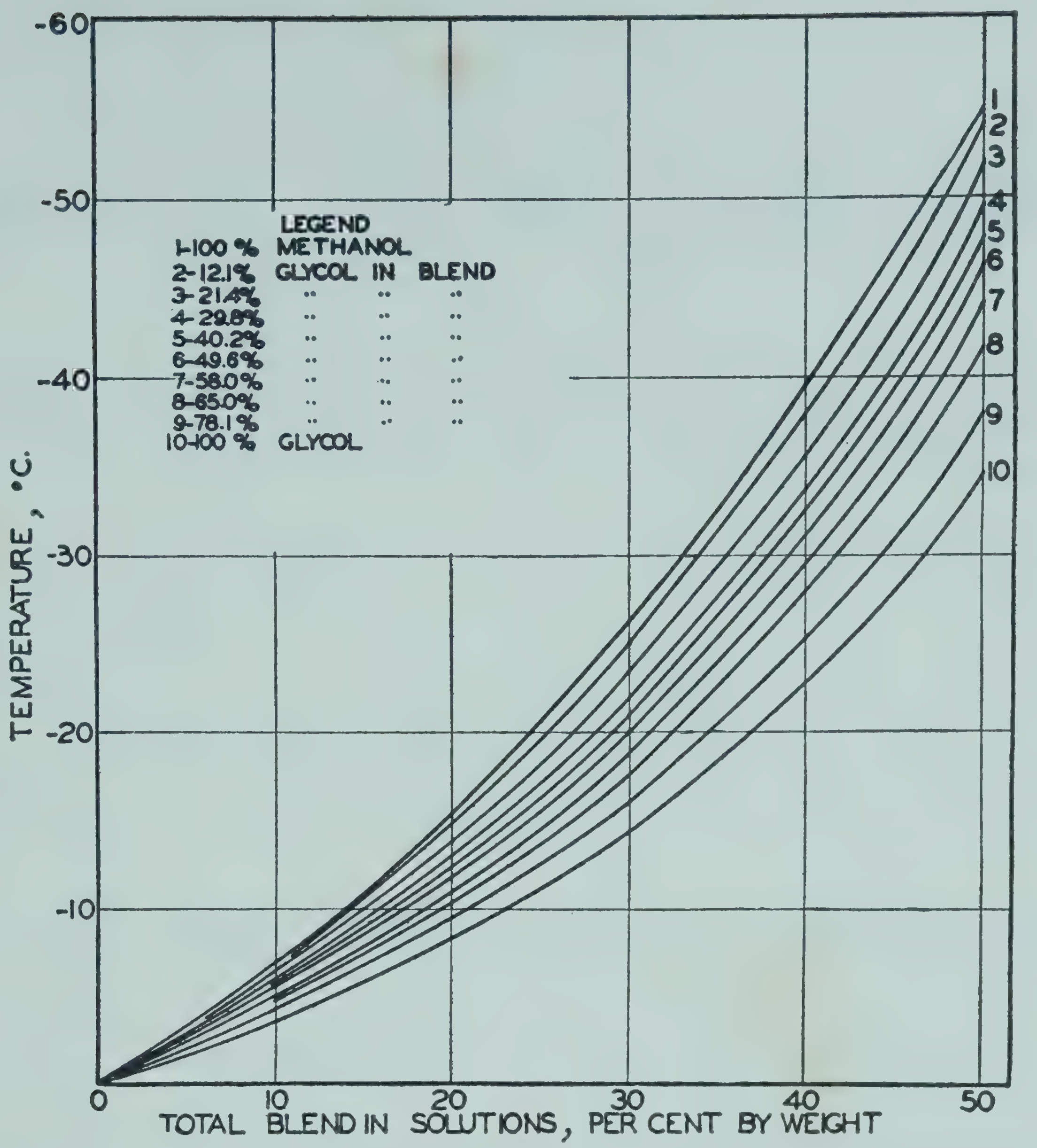


FIGURE 11.58. Freezing Points of Aqueous Blend Solutions.

The glycols are colorless, odorless liquids having good solvent properties for resins, essential oils, gums, and dyes. Some glycols are also used in hydraulic brake fluid formulations. Because of their solvency, the glycols are used as mutual solvents, thus bringing about homogeneous systems of immiscible components. They are also widely used as chemical intermediates for making synthetic resins, explosives and emulsifying agents.

Some use has been made of the glycols in pharmaceutical preparations, particularly propylene glycol owing to its low degree of toxicity. In such preparations, they function as vehicles, preservatives and in emulsifying agents.

During the last twenty years, six different glycols have grown from the laboratory phase to tank car quantities. At the same time about fifty glycol derivatives have also become commercially available. Table 11.14 lists the physical properties of the more important industrial glycols and their derivatives.

Ethylene Glycol (glycol, 1,2-ethanediol) ($HOCH_2CH_2OH$). Wurtz[11] was the first to prepare ethylene glycol, but it was not until 1925 that it

TABLE 11.14. PHYSICAL PROPERTIES OF INDUSTRIAL GLYCOLS AND THEIR DERIVATIVES.[10]

NAME	FORMULA	MOL. WT.	SP. GR. 20/20° C.	BOILING PT., 760 MM. ° C.	VAPOR PRESSURE, 20° C. Mm. Hg	FLASH PT. ° F.	POUNDS PER GAL., 20° C.	SOLUBILITY, % BY WT. AT 20° C. In water	Water in
Ethylene glycol	$HOCH_2CH_2OH$	62.07	1.1155	197.2	0.12	240	9.3	Miscible	Miscible
Diethylene glycol	$HOCH_2CH_2OCH_2CH_2OH$	106.12	1.1184	244.8	0.01	290	9.3	Miscible	Miscible
Triethylene glycol	$HOC_2H_4OC_2H_4OC_2H_4OH$	150.17	1.1254	287.3	<0.01	330	9.4	Miscible	Miscible
Tetraethylene glycol	$HO(C_2H_4O)_3C_2H_4OH$	194.14	1.1261	327.3	<0.001	345	9.4	Miscible	Miscible
Propylene glycol	$CH_3CHOHCH_2OH$	76.09	1.0381	188.2	0.18	225	8.7	Miscible	Miscible
Dipropylene glycol	$(CH_3CHOHCH_2)_2O$	134.17	1.0252	231.8	0.03	280	8.5	Miscible	Miscible
1,3-Butylene glycol	$CH_3CH(OH)CH_2CH_2OH$	90.08	1.0259	203.5	..	...	8.6	Miscible	Miscible
Industrial Ether Derivatives of Glycols									
Methyl Cellosolve	$CH_3OCH_2CH_2OH$	76.09	0.9664	125.0	8.0	115	8.0	Miscible	Miscible
Diethyl Cellosolve	$C_2H_5OCH_2CH_2OC_2H_5$	118.17	0.8424	121.4	12.0	95	7.0	21.0	3.43
Cellosolve solvent	$C_2H_5OCH_2CH_2OH$	90.12	0.9311	135.0	3.72	130	7.8	Miscible	Miscible
Butyl Cellosolve	$C_4H_9OCH_2CH_2OH$	118.17	0.9019	171.2	0.97	165	7.5	Miscible	Miscible
Phenyl Cellosolve	$C_6H_5OCH_2CH_2OH$	138.16	1.1094	244.7	0.03	250	9.2	2.67	10.83
Benzyl Cellosolve	$C_6H_5CH_2OCH_2CH_2OH$	152.19	1.0700	255.9	0.02	265	8.9	0.43 (23° C.)	18.1 (25° C.)
Methyl Carbitol	$CH_3OCH_2CH_2OCH_2CH_2OH$	120.15	1.0354	193.2	0.19	200	8.6	Miscible	Miscible
Diethyl Carbitol	$(C_2H_5OCH_2CH_2)_2O$	162.23	0.9094	187.9	0.50	180	7.6	Miscible	Miscible
Carbitol solvent	$C_2H_5OCH_2CH_2OCH_2CH_2OH$	134.17	0.9898	201.9	0.22	210	8.2	Miscible	Miscible
Butyl Carbitol	$C_4H_9OCH_2CH_2OCH_2CH_2OH$	162.23	0.9554	230.7	0.06	240	7.9	Miscible	Miscible
Dimethoxytetraglyco	$(CH_3OC_2H_4OC_2H_4)_2O$	222.28	1.0132	275.8	<0.01	285	8.4	Miscible	Miscible
Industrial Ester Derivatives of Glycols									
Methyl Cellosolve acetate	$CH_3COOCH_2CH_2OCH_3$	118.13	1.0067	144.5	3.73	140	8.4	Miscible	Miscible
Cellosolve acetate	$CH_3COOCH_2CH_2OC_2H_5$	132.16	0.9749	156.3	1.09	140	8.1	23.0	6.0
Glycol diacetate	$(CH_3COO)_2C_2H_4$	146.14	1.1063	190.5	0.38	220	9.2	16.44	6.97
Carbitol acetate	$CH_3COOC_2H_4OC_2H_4OC_2H_5$	176.11	1.0114	217.7	0.15	230	8.4	Miscible	Miscible
Butyl Carbitol acetate	$CH_3CO(OC_2H_4)_2OC_4H_9$	204.26	0.9871	245.8	0.03	240	8.2	3.8	2.7
Industrial Nitrogen Derivatives of Glycols									
Ethylene diamine	$NH_2CH_2CH_2NH_2$	60.10	0.8995	117.2	11.0	110	7.5	Miscible	Miscible
Diethylene triamine	$NH_2C_2H_4NHC_2H_4NH_2$	103.17	0.9542	206.7	0.22	215	7.9	Miscible	Miscible
Triethylene tetramine	$NH_2(C_2H_4NH)_2C_2H_4NH_2$	146.24	0.9816	277.9	0.01	260	8.2	Miscible	Miscible
Monoethanolamine	$HOCH_2CH_2NH_2$	61.08	1.0179	170.5	0.48	200	8.5	Miscible	Miscible
Diethanolamine	$(HOCH_2CH_2)_2NH$	105.14	1.0985	268.0	<0.01	280	9.1	Miscible	Miscible
Triethanolamine	$(HOCH_2CH_2)_3N$	149.19	1.1258	244.0[a]	<0.01	365	9.4	Miscible	Miscible
Phenyl diethanolamine	$C_6H_5N(CH_2CH_2OH)_2$	181.13	Solid	Melts 58	<0.1	...	10.0	3.34	.....
Ethyl phenyl ethanolamine	$C_6H_5N(C_2H_5)CH_2CH_2OH$	165.13	1.04	268	..	...	8.7	0.50	.....
Phenyl ethanolamine	$C_6H_5NHCH_2CH_2OH$	137.10	1.09	286.0	<0.1	...	9.1	4.58	15.3
Monoisopropanolamine	$CH_3CHOHCH_2NH_2$	75.08	0.9810	45[b]	..	...	8.2	Miscible	Miscible
Triisopropanolamine	$(CH_3CHOHCH_2)_3N$	191.18	1.0196	144[b]	<0.1	305	8.5	Miscible	Miscible
Diethylaminoethanol	$(C_2H_5)_2NC_2H_4OH$	117.13	0.8851	162.2	1.4	140	7.4	Miscible	Miscible
Hydroxyethyl ethylene diamine	$H_2NCH_2CH_2NHCH_2CH_2OH$	104.12	....	...	..	...	...	Miscible	Miscible
Tetraethylene pentamine	$NH_2(CH_2CH_2NH)_3CH_2CH_2NH_2$	189.22	0.9994	333.0	<0.01	...	8.3	Miscible	Miscible
Industrial Chlorine Derivatives of Glycols									
Ethylene chlorohydrin	$HOCH_2CH_2Cl$	80.52	1.2045	128.7	5.8	140	10.0	Miscible	Miscible
Propylene chlorohydrin	$CH_3CHOHCH_2Cl$	94.54	1.1128	127.4	6.87	125	9.3	Miscible	Miscible
Diglycol chlorohydrin	$ClCH_2CH_2OCH_2CH_2OH$	190.19	1.1698	196.8	0.17	225	9.7	Miscible	Miscible
Ethylene dichloride	$ClCH_2CH_2Cl$	98.97	1.2555	83.5	61.1	70	10.5	0.86	0.5
Propylene dichloride	$CH_3CHClCH_2Cl$	112.99	1.1593	95.9	3.75	70	9.7	0.26	0.07
Triglycol dichloride	$ClC_2H_4(OC_2H_4)_2Cl$	187.07	1.1974	241.3	0.06	250	9.9	1.89	0.83
Dichloroethyl ether	$ClCH_2CH_2OCH_2CH_2Cl$	143.02	1.2220	178.5	1.0	185	10.1	1.07	0.28
Dichloroisopropyl ether	$[CH_3CH(CH_2Cl)]_2O$	171.07	1.1122	187.3	0.85	185	9.3	0.17	0.11

[a] At 50 mm.

[b] At 5 mm.

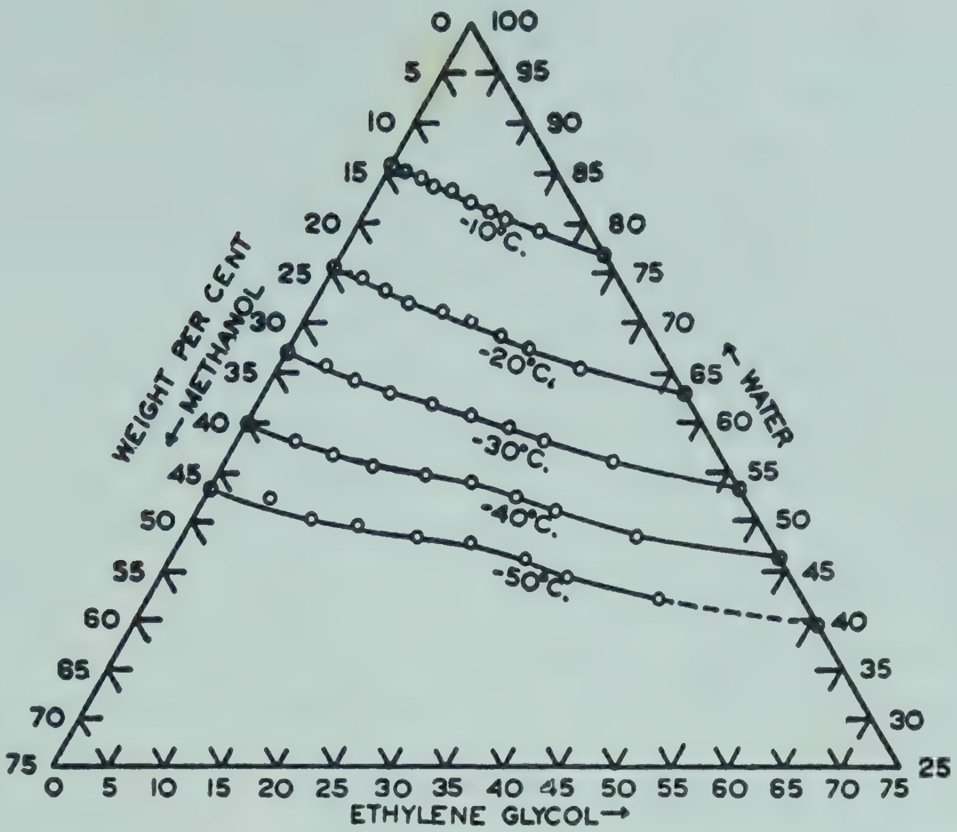


FIGURE 11.59. Freezing Points of Aqueous Ethylene Glycol-Methanol Solutions.

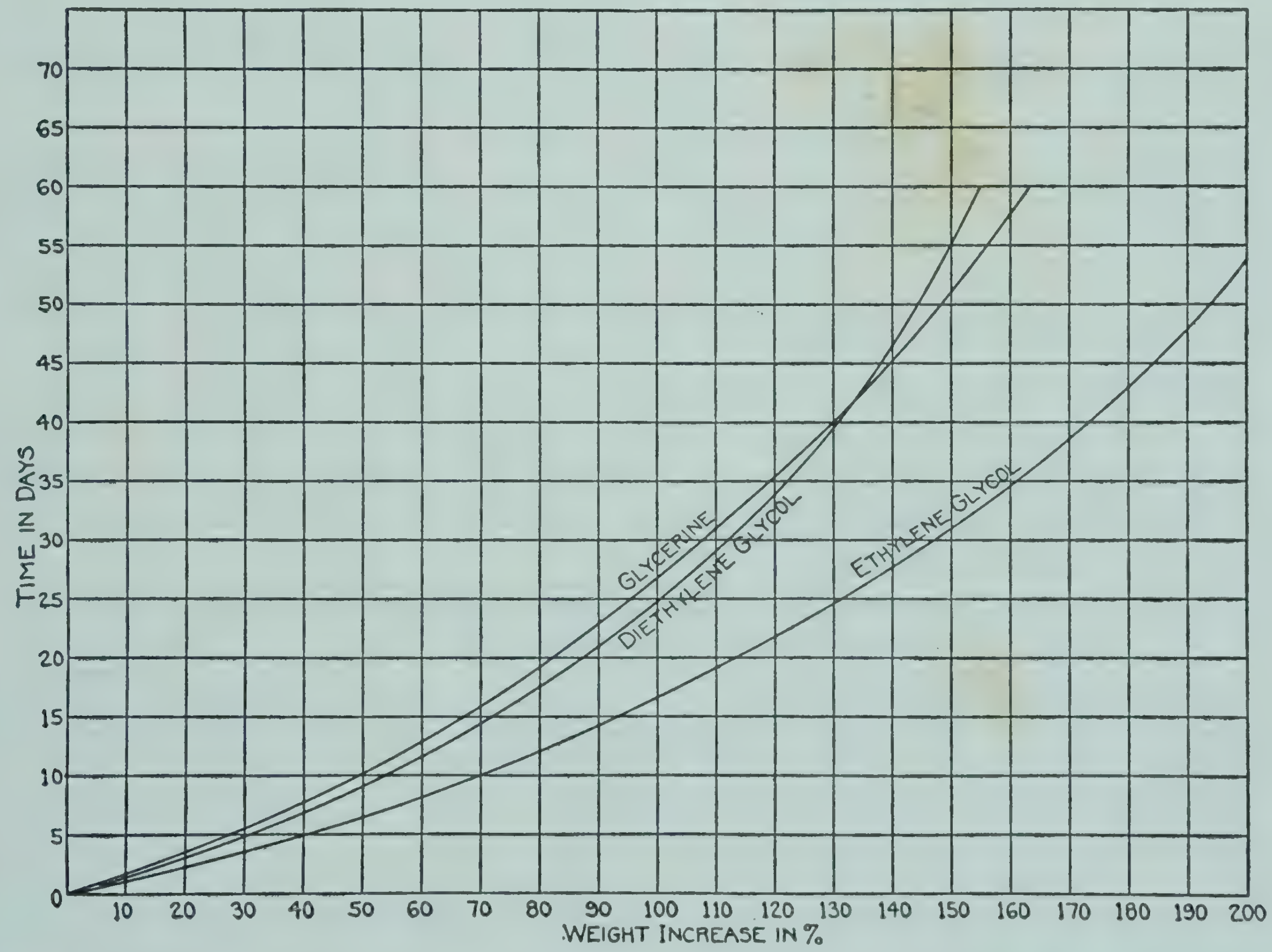


FIGURE 11.60. Comparative Hydroscopicities of Ethylene Glycol, Diethylene Glycol and Glycerine. Saturated Atmosphere at 25°C.[6]

became commercially[12] available in the United States. It is a colorless, nearly odorless liquid with a sweetish taste, and its physical properties lie midway between those of ethyl alcohol and glycerol. It is hygroscopic to a high degree, absorbing twice its weight of water at 100 per cent relative humidity. This property therefore makes it an excellent moistening agent[13]. It is miscible in all proportions with water, alcohols, ketones, etc. It is slightly miscible with hydrocarbons and raw linseed oil, partly soluble in shellac and rosin. Ethylene glycol will not dissolve nitrocellulose, cellulose acetate, vinyl resins, kauri gum, dewaxed dammar, ester gum, and unvulcanized rubber. It will dissolve certain types of dyes.

Its many and varied[10, 14] uses are listed in the table below. Second only to antifreeze is its use in the manufacture of glycol dinitrate, which is employed in low-freezing dynamites. The primary use of ethylene glycol is as a nonvolatile antifreeze, as a result of its ability to lower the freezing point of water without sacrifice of the cooling effect of water. It is indeed used as a high-temperature coolant in aircraft engines[15] and also in truck motors designed for heavy service at desert temperatures.

*Uses of Ethylene Glycol**

Use	*Amount*	*Per cent*
Total Allocations	189,169	100.0
Export[1]	32,850	17.4
Other uses	156,319	82.6
Antifreeze[2]	119,874	63.4
Explosives	14,843	7.8
Cellophane	6,650	3.5
Coolants	6,192	3.3
Chemicals and synthetic resins	3,826	2.0
Hydraulic brake fluid[3]	3,202	1.7
Radio condenser fluid	538	0.3
Textiles and rayon	140	0.1
Miscellaneous uses and small orders[4]	1,054	0.5

[1] Excludes Canada; see note [2].

[2] Includes military requirements plus a small amount for undesignated purposes and all civilian and Canadian antifreeze assignments.

[3] Includes de-icing preparations.

[4] Includes ethylene glycol used for drugs and cosmetics; for wood stains, molding-sand binders, cutting oils, and gas and air dehydration.

* "Facts for Industry," Bureau of the Census.

Its hygroscopic and solvent properties are utilized in dye pastes, in printing, in glue mixtures, in dyeing of leather, in textile processing and cellophane manufacture. It has been found useful as a solvent for dyes[16] used in quick-drying wood stains. It is used in conjunction with methanol and the resulting stains are fast to light, dry rapidly, possess brilliancy, do not bleed, and cause no raising of the grain. Other uses for this solvent are in the production of alkyd resins and synthetic fibers.

Although ethylene glycol is an excellent agent for lowering the freezing point of water, Conrad, Hill, and Ballman[16] have worked out mixtures of methanol and ethylene glycol which though more volatile are less costly. The freezing points of aqueous methanol, ethylene glycol, and methanol-ethylene glycol mixtures are given in the following tables and graphs.

Cragol[17] of the National Bureau of Standards has compiled an exhaustive report on the properties of ethylene glycol and its aqueous solutions.

Typical Properties and Specifications

Apparent ignition temperature in air	417°C
Boiling point	197.2°C
Coefficient of expansion	$Vt = 1 + 0.0005657\ t$
Electrical conductivity at 25°C	1.07×10^{-6} recip. ohms
Fire point	120°C
Flash point	116°C
Freezing point	−12.3°F
Heat of combustion	
Constant pressure	282,200 cal./g. mol
Constant volume	281,400 cal./g. mol
Heat of dilution $[C_2H_4(OH)_2.{}_2H_2O$	0.06 cal./g
Heat of fusion	44.76 cal./g
Latent heat of vaporization at 130.6°C	235.5 cal./g
160.3	282.2 cal./g
188.4	210.3 cal./g
Specific gravity at 20/20°C	1.1150–1.1158
Refractive index at 20°C	1.4311
Specific heat at −9.8°C	0.537
5.2	0.556
15	0.571
20	0.575
Surface tension at 25°C	52.5 dynes/cm
Vapor pressure at 20°C	0.12 mm
Viscosity at 15°C	0.26 poise
20	0.21 poise
25	0.17 poise
Weight per gallon at 20°C	9.28 lbs.
Acidity (as acetic)	0.01% max.
Boiling range	
Above 210°C	None
Below 190	None
Below 195	Not more than 5%
Below 202	Not less than 95%
Water content	Not more than 0.5% by wt.

Propylene Glycol (Propanediol 1,2; 1,2-Dihydroxypropane, Methyl Glycol) ($CH_3 \cdot CHOH \cdot CH_2OH$). Propylene glycol was first synthesized in 1859, but its commercial production did not begin until 1932. Since that time, however, it has grown in increasing importance among the family of glycols. It is a stable, water-white, hygroscopic, viscous liquid, miscible with water, alcohols, chloroform, acetone, and many organic solvents.

TABLE 11.15. FREEZING POINTS OF AQUEOUS SOLUTIONS

GLYCOL FREEZING POINT				METHANOL FREEZING POINT				
% by weight glycol	Olsen, Brunjes, Olsen (*11*) °C	Curme and Young (*2*), °C.	Present work, °C.	% by weight methanol	I. C. T. (*7*), °C	Aldrich and Querfeld (*1*), °C	Feldman and Dahlstrom (*4*), °C	Present work, °C
10	−3.3	−2.5	−3.6	10	−6.6	−6.0	−6.3	−6.8
20	−7.8	−7.7	−8.3	20	−15.4	−14.2	−15.2	−15.3
30	−13.5	−13.9	−14.4	25	−20.8	−19.0	−20.7	−20.7
35	−17.1	−18.6	−18.2	30	−26.4	−24.7	−26.5	−26.3
40	−22.1	−23.3	−22.6	35	−32.6	−30.5	−33.1	−33.0
50	−35.4	−33.9	−34.6	40	−39.5	−37.5	−39.8	−39.7
60	−46	−46.4	−49.3	50	−55.6			−54.9
100		−11.6	−13.5					

TABLE 11.16. FREEZING POINTS OF ETHYLENE GLYCOL-METHANOL BLENDS IN AQUEOUS SOLUTIONS

BLEND		F. P., WITH FOLLOWING % BY WT. OF TOTAL BLEND IN AQUEOUS SOLUTION:				
Ethylene glycol	Methanol	10 °C	20 °C	30 °C	40 °C	50 °C
% by weight						
100.0	0	−3.6	−8.3	−14.4	−22.6	−34.6
78.1	21.9	−4.2	−9.6	−16.1	−25.4	−37.9
65.0	35.0	−4.8	−10.2	−17.7	−28.0	−41.6
58.0	42.0	−5.0	−10.8	−18.9	−29.4	−44.1
49.6	50.4	−5.5	−11.7	−20.1	−31.1	−46.5
40.2	59.8	−5.7	−12.2	−21.0	−32.3	−47.7
29.8	70.2	−5.9	−12.9	−22.0	−33.6	−49.6
21.4	78.6	−6.3	−13.8	−23.6	−35.4	−52.0
12.1	87.9	−6.5	−14.8	−25.0	−37.9	−54.0
0	100.0	−6.8	−15.3	−26.3	−39.7	−54.9

TABLE 11.17. SOLUBILTIES OF FLAVORING MATERIALS IN VARIOUS SOLVENTS

Flavoring	Temp. °C	95% Ethyl Alcohol	Propylene Glycol	Glycerine
Oil of Orange	30	0.5%	0.3%	0.4%
	25	3.03%	0.26%	0.35%
Oil of Lemon	30	60.0%	0.6%	0.4%
	25	65.90%	0.81%	0.59%
Benzaldehyde	30	50.0%	50.0%	2.44%
	25	Completely Miscible	Completely Miscible	3.56%
Vanillin	25	44.35%	21.65%	*4.59%
	25	47.15%	23.10%	4.38%
Coumarin	25	17.82%	7.18%	*0.80%
	25	18.65%	6.77%	0.80%

* 30°C.

Table 11.18. Solubilities of Aromatic Chemicals in Propylene Glycol/Water Mixtures at 25°C[21]

AROMATIC CHEMICALS	% BY VOLUME OF TOTAL MIXTURE				
% Propylene Glycol	100	80	60	40	20
Aldehyde C-9	misc.	1.85	0.40	insol.	insol.
Aldehyde C-10	3.45	0.12	insol.	insol.	insol.
Aldehyde C-12	1.85	0.40	insol.	insol.	insol.
Aldehyde C-14 (so called)	misc.	1.20	0.44	0.08	0.08
Aldehyde C-16 (so called)	misc.	1.30	1.00	insol.	insol.
Aldehyde C-18 (so called)	misc.	4.30	2.00	0.45	0.20
Amyl Acetate	misc.	3.00	1.84	0.40	0.24
Amyl Butyrate	6.90	1.15	0.50	0.08	0.08
Amyl Formate	misc.	7.70	1.70	0.65	0.48
Amyl Propionate	8.80	1.70	0.56	0.24	0.16
Amyl Valerate	4.00	0.75	0.24	0.08	0.06
Anethol	2.12	0.70	0.12	insol.	insol.
Benzaldehyde	misc.	misc.	3.20	1.84	0.80
Benzylacetate	misc.	6.45	2.16	0.64	0.36
Benzylbutyrate	6.50	1.60	0.64	0.20	0.16
Caproic Acid	misc.	misc.	misc.	misc.	1.40
Cinnamic Aldehyde	misc.	4.05	1.00	0.50	0.32
Citral	misc.	3.38	1.00	0.25	0.10
Coumarin	6.85	4.15	2.05	0.40	0.25
Ethyl Acetate	misc.	misc.	misc.	8.75	4.65
Ethyl Anthranilate	misc.	misc.	2.30	0.50	0.04
Ethyl Benzoate	4.90	2.60	1.30	0.64	insol.
Ethyl Isobutyrate	misc.	1.96	0.96	0.85	0.12
Ethyl Caproate	8.20	2.20	0.60	0.20	0.14
Ethyl Capryllate	4.20	0.98	0.40	0.20	0.08
Ethyl Cinnamate	5.80	1.48	0.90	insol.	insol.
Ethyl Propionate	misc.	9.80	5.90	2.35	1.40
Ethyl Valerate	misc.	4.05	1.05	0.04	insol.
Ethyl Vanillin	misc.	misc.	5.80	1.95	0.80
Ionone A	misc.	1.32	0.16	0.04	insol.
Ionane B	misc.	1.56	0.24	insol.	insol.
Isobutyl Acetate	misc.	7.50	1.56	0.96	0.64
Isobutyl Butyrate	9.00	1.40	0.65	0.16	0.14
Isobutyl Caproate	2.20	0.30	0.08	insol.	insol.
Isobutyl Cinnamate	3.20	0.80	0.35	insol.	insol.
Methyl Anthranilate	misc.	misc.	2.95	0.80	0.32
Oeanthic Ether	1.05	0.40	0.06	0.04	0.04
Tolyl Acetate	misc.	2.20	0.75	in suspension	
Tolyl Aldehyde	misc.	1.96	0.94	0.40	0.36
Phenylacetic Aldehyde	misc.	0.80	0.60	in suspension	
Propyl Acetate	misc.	misc.	7.40	3.00	1.25
Valeric Acid	misc.	misc.	misc.	misc.	4.40
Vanillin	misc.	misc.	misc.	3.10	1.20

TABLE 11.19. SOLUBILITIES OF ESSENTIAL OILS IN PROPYLENE GLYCOL/WATER MIXTURES AT 25°C.[21]

ESSENTIAL OILS	% BY VOLUME IN TOTAL MIXTURE				
% Propylene Glycol	100	80	60	40	20
Angelica Root	2.80	2.18	0.64	0.56	0.38
Bitter Almond	over 10%	misc.	2.30	2.00	0.80
Caraway	7.70	2.25	0.44	0.32	0.04
Cassia	over 10% misc.	9.10	1.15	0.28	0.10
Celery Seed	2.72	1.00	0.60	0.20	0.16
Clove	over 10% misc.	9.45	2.05	0.40	0.20
Cognac	over 10% misc.	0.65	0.45	0.22	0.22
Coriander	over 10% misc.	4.45	0.60	0.16	0.12
Dillseed	8.20	2.60	0.50	0.28	0.20
Dillweed	3.80	1.70	0.15	0.12	0.04
Fennel	5.60	1.25	0.40	0.16	0.12
Juniper	1.92	0.84	0.24	insol.	insol.
Lemon	0.80	0.55	0.35	0.10	insol.
Lemongrass	9.98	3.65	0.40	0.28	0.24
Mandarin	1.33	0.24	0.16	0.16	0.12
Marjoram	3.76	1.90	0.90	0.24	0.20
Nutmeg	2.40	0.95	0.50	0.25	0.12
Orange	0.25	0.15	0.10	0.05	insol.
Peppermint	over 10% misc.	6.60	0.88	0.04	insol.
Pimento Berries	9.95	4.50	2.70	0.70	0.55
Rue	7.20	0.85	0.20	0.12	0.02
Sage	9.70	3.30	1.15	0.16	0.14
Sassafras	3.40	1.10	0.35	1.12	0.08
Spearmint	over 10% misc.	3.20	1.50	0.35	0.15
Sweet Birch	6.60	2.05	0.36	0.20	insol.
Thyme	9.80	3.20	1.30	0.32	0.20
Wintergreen	6.90	1.90	0.40	0.20	insol.

Propylene glycol is outstanding in that it is the only glycol approved at present for use in preparations intended for internal consumption. The Food and Drug Administration has ruled that it is not a harmful ingredient in food products or cosmetics. Hence it is used as a solvent for flavors i many types of confectionery and bakery products.

Propylene glycol is slightly soluble in hydrocarbons, raw linseed oi partly miscible with shellac and kauri gum, and does not dissolve nitrocellulose, cellulose acetate, vinyl resins, dewaxed dammar, ester gum, an

Table 11.20. Solubility of Pharmaceutical Products in Propylene Glycol*[21]

	INDICATION OF SOLUBILITY IN PROPYLENE GLYCOL
1. DRUGS AND MEDICINALS	
Sulfanilamide	10%
Sulfathiazole	3%
Sulfapyridine	3%
Sulfadiazine	0.3%
Antipyrine	20%
Sodium Iodobismuthite	6%
Sodium Bismuth Thioglycolate	9.4%
Phenobarbital (Luminal Sodium)	Soluble
Paraldehyde	Very soluble
2. LOCAL ANESTHETICS	
Diathane	5%
Benzocaine	Very soluble dilute aqueous solutions
Salicyl Alcohol (Saligenin)	4%
Benzyl Alcohol	20%
3. ANTISEPTICS	
Hexylresorcinol	Soluble
Thymol	Soluble
Menthol	<50%
Camphor	9.8%
Trichlor-tert, butanol	<60.0%
Chlorothymol	Soluble
4. VITAMINS AND HORMONES	
Vitamin A	Soluble
Vitamin D	Soluble
a-Estradiol	0.5 mq. per cc.
Desoxycorticosterone Acetate	Soluble
Stilbestrol	Soluble
5. ORGANIC SUBSTANCES	
Phenothiazine	Soluble
6. INORGANIC SUBSTANCES	
Bismuth Hydroxide	Soluble

* See Bulletin of the National Formulary Committee, Vol. XI, Nos. 5–6, May–June, 1943, pps. 91–98 and XI, Nos. 9–10, Sept.–Oct., 1943 pps. 184–186.

unvulcanized rubber. The accompanying tables show propylene glycol as an excellent solvent for many flavors, essential oils and pharmaceutical products. Compared with glycerol, propylene glycol is in many instances a superior general solvent. It is also comparable to ethyl alcohol in its preservative power. Propylene glycol is used in tobacco as a hygroscopic and blending agent and as a diluent in castor oil base, hydraulic brake fluid compositions, as a coolant and antifreeze to replace corrosive brines,

TABLE 11.21. SOLUBILITIES OF FLAVORING MATERIALS IN PROPYLENE GLYCOL-WATER MIXTURES[21]

(Temperature 25° C.)

FLAVORING MATERIAL	PER CENT GYLCOL				
	100	80	60	40	20
	Per cent Flavoring by Weight in Total Mixture				
Amyl Acetate	Misc.	Misc.	Misc.	1.48	1.34
Iso-Amyl Formate	Misc.	5.22	4.51	1.68	1.53
Benzaldehyde	Misc.	18.97	4.62	1.80	0.82
Cassia Oil	Misc.	3.13	0.85	0.69	0.21
Citral	Misc.	0.35	0.17	0.10	0.04
Clove Oil	Misc.	1.19	0.26	0.24	0.12
Ethyl Acetate (99%)	Misc.	Misc.	Misc.	11.65	8.09
Ethyl Formate	Misc.	Misc.	Misc.		17.45
Eucalyptol	19.90	4.75	1.73	0.35	0.25
Lemon Oil	0.81	0.52	0.32	0.13	0.03
Nutmeg Oil	1.53	0.34	0.17	0.14	0.11
Orange Oil	0.26	0.13	0.08	0.06	0.03
Phenyl Ethyl Alcohol	Misc.	Misc.	Misc.	18.95	3.11
Sassafras Oil	2.02	1.21	0.20	0.12	0.08
Coumarin	7.70	5.05	2.30	0.50	0.32
Vanillin	20.20	20.10	12.60	5.85	2.09
Ethyl Vanillin	14.20	10.80	5.20	1.84	0.79
Methyl Salicylate	17.05				
Methyl Anthranilate	Misc.	Misc.	Misc.		

and as a plasticizer in adhesives and cellulose products, in dyes, inks’ leather, paints, paper, resins, and film. A pharmaceutical grade meeting National Formulary Specifications is also available.

Typical Properties and Specifications

Boiling point	188.2°C
Coefficient of expansion per °C	0.000695 to 20°C 0.000743 to 55°C
Flash point (ASTM Open Cup)	99°C
Heat of combustion	431.0 kg. cal./mole
Latent heat of evaporation at B.P.	168.6 cal./g.
Specific gravity at 20/20°C	1.037–1.040
Refractive index at 25°C	1.4300–1.4310
Specific heat at 20°C	0.590 cal./g.
Surface tension at 25°C	40.1 dynes/cm
Vapor pressure at 20°C	0.18 mm
Viscosity at 25°C	0.406 poise
Weight per gallon at 20°C	8.64 lbs.
Acidity (as acetic)	0.01% by wt. (max.)
Distillation range at 760 mm (regular grade)	180–210°C
Heavy metals (N.F. grade)	5 ppm max.
Residue	0.007% by wt.

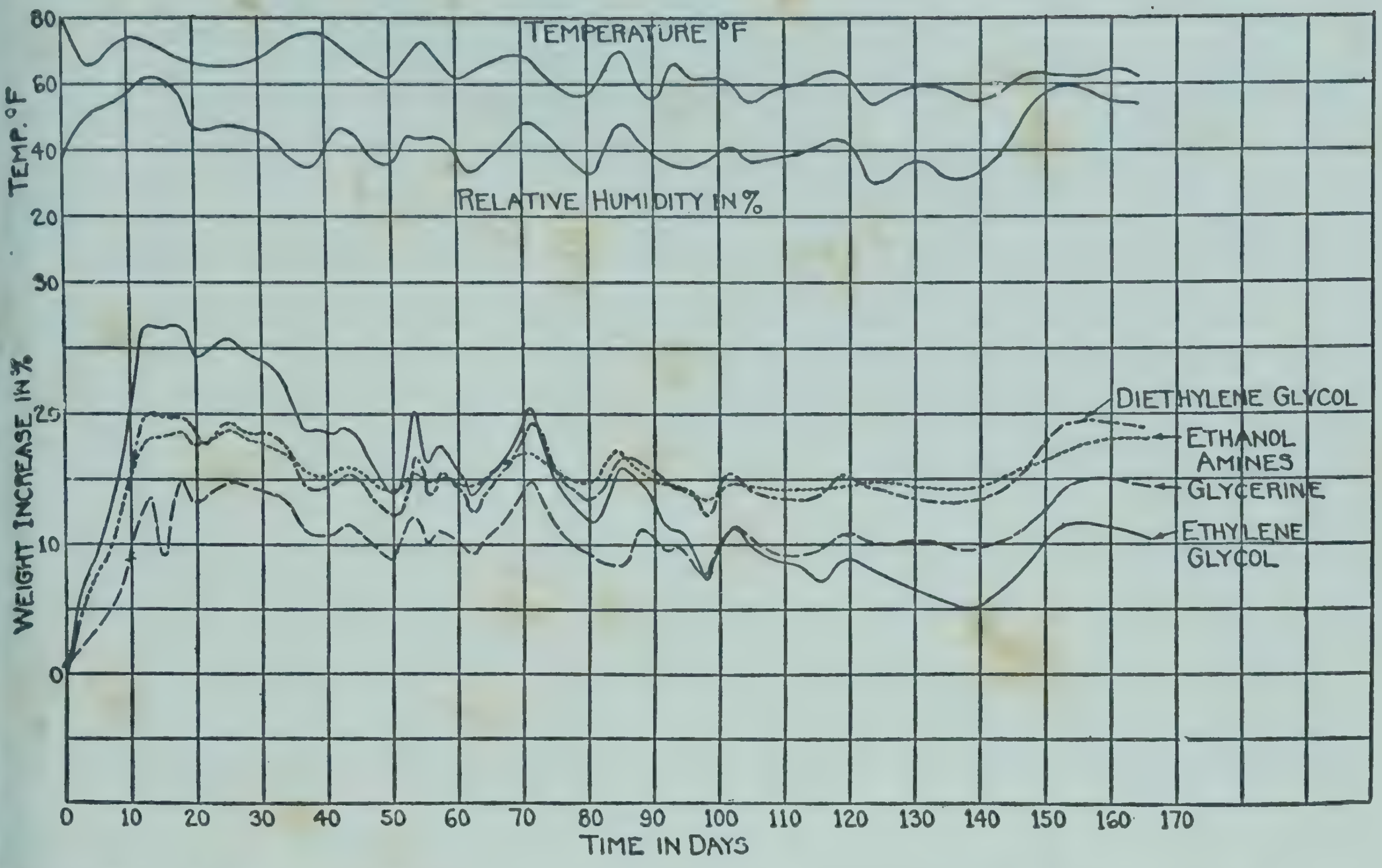


FIGURE 11.61. Comparative Hydroscopicities, Atmospheric Temperatures, and Humidities.[6]

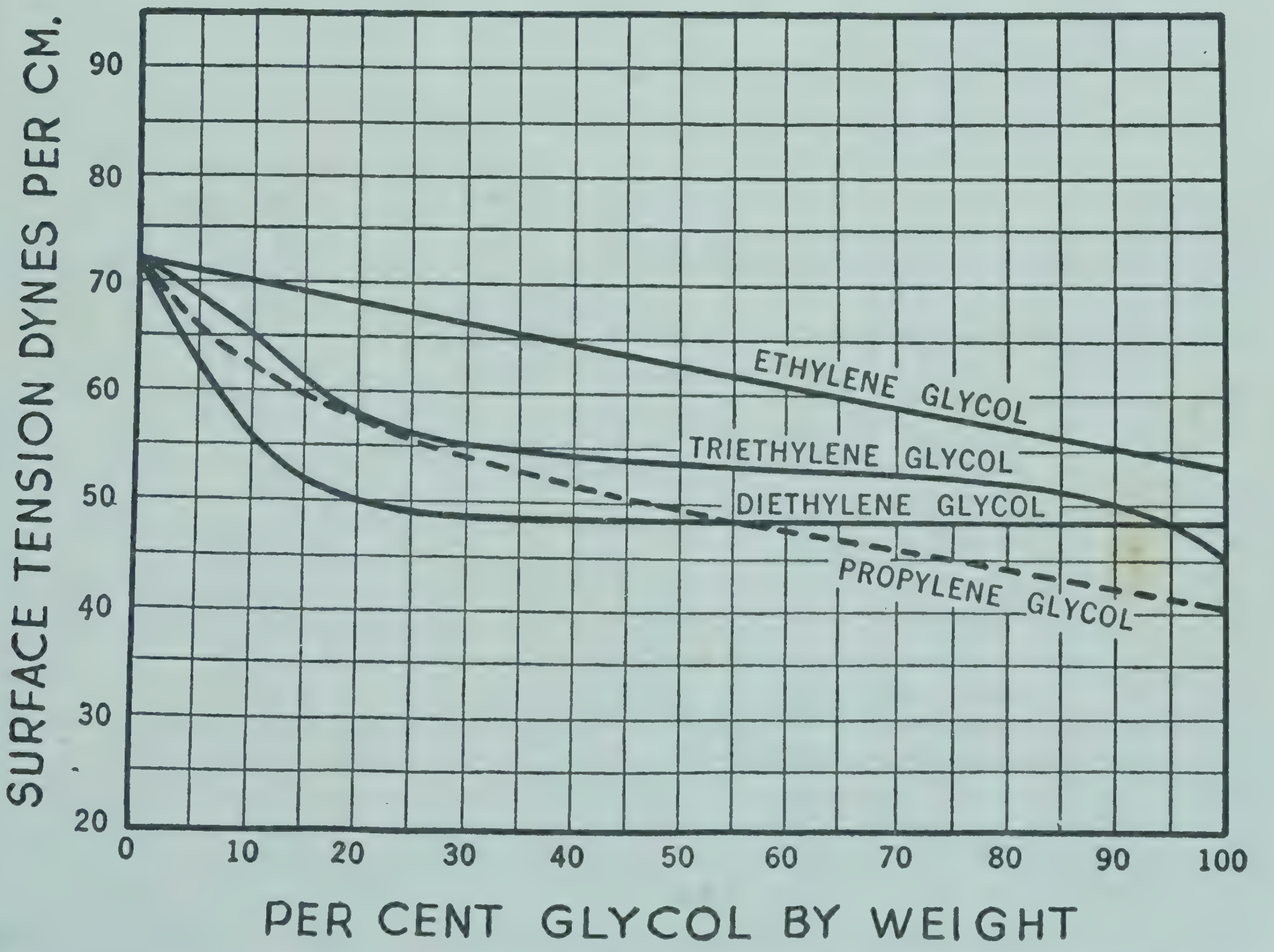


FIGURE 11.62. Surface Tension of Aqueous Solutions at 25°C. (Du Noüs apparatus, Water equal to 72 dynes per cm.)[6]

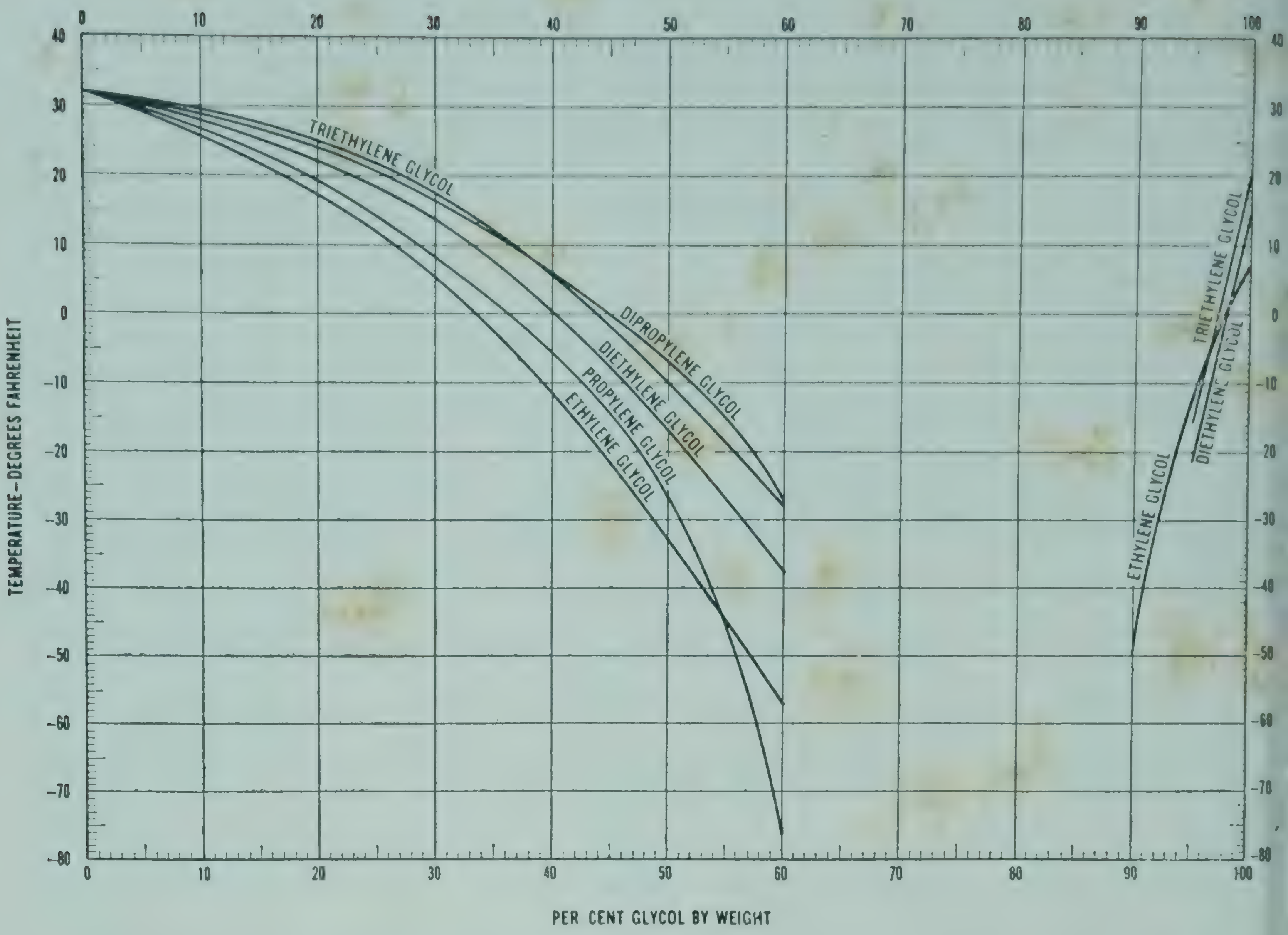


FIGURE 11.63. Freezing Points of Aqueous Solutions of Various Glycols.[18]

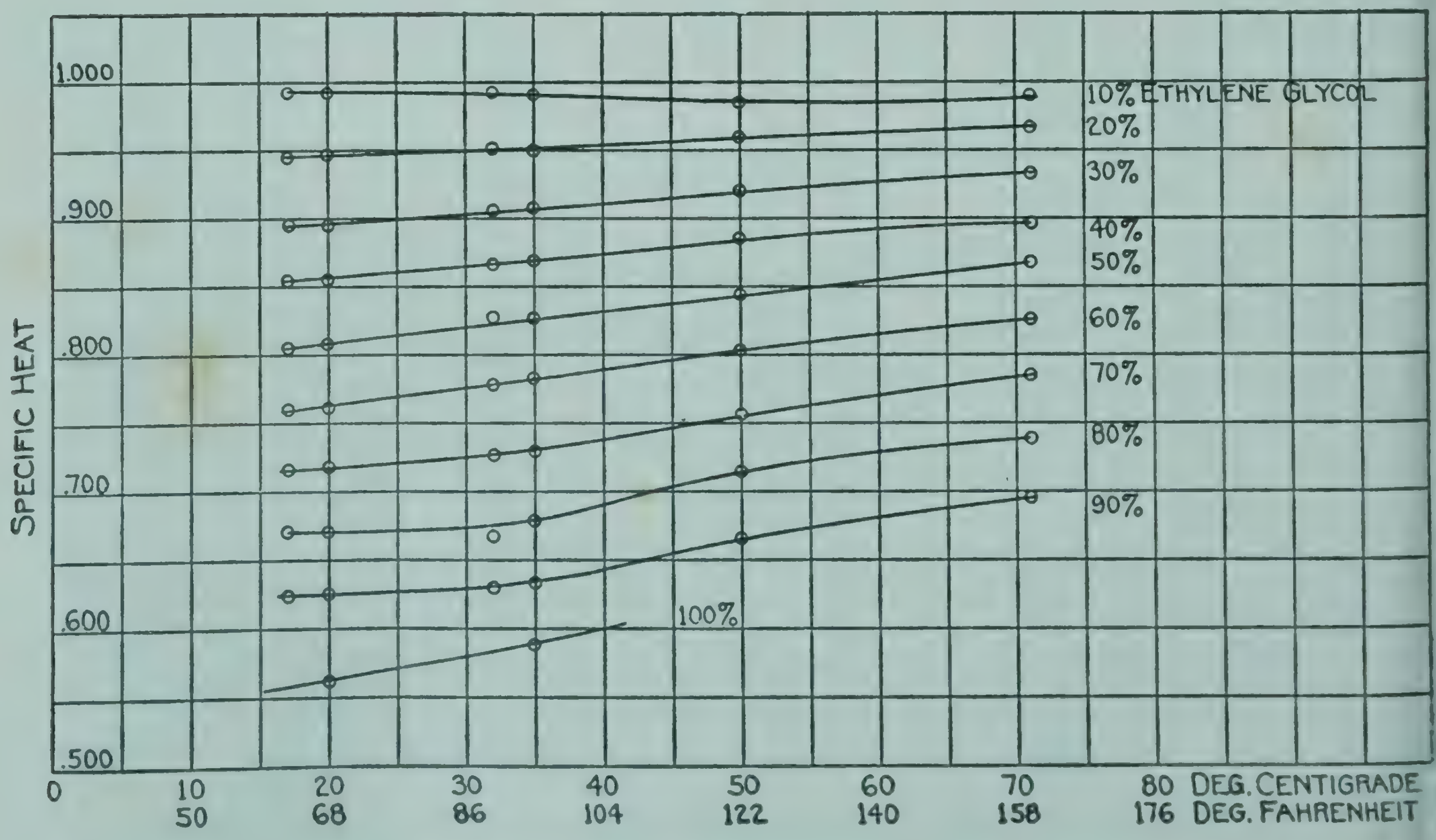


FIGURE 11.64. Specific Heat of Ethylene Glycol-Water Solutions.[6]

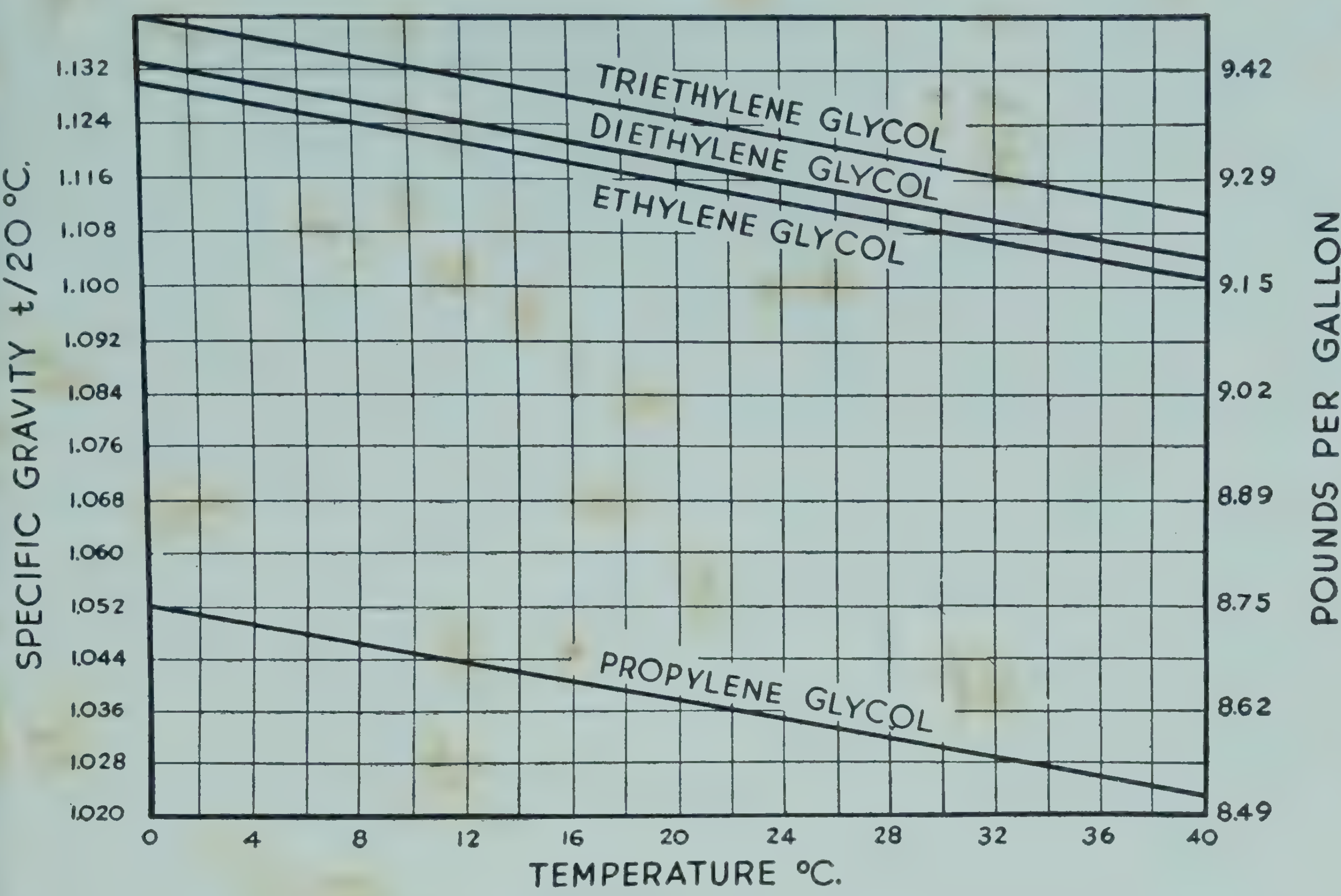


Figure 11.65. Specific Gravity and Weight per Gallon at Various Temperatures.[6]

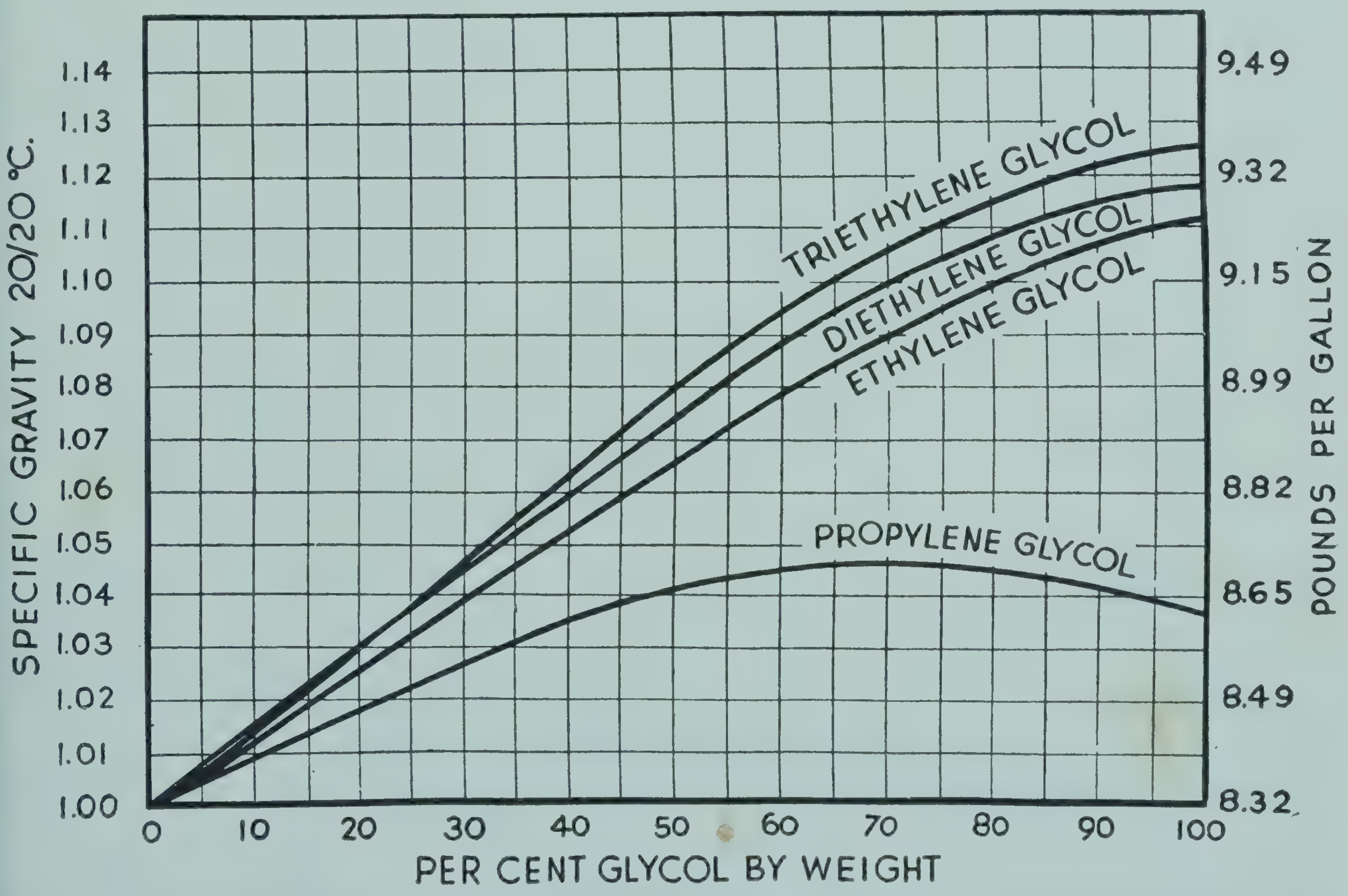


Figure 11.66. Specific Gravity and Weight per Gallon of Aqueous Solutions at 20°C.

Diethylene Glycol (2,2′-Oxydiethanol, Di-2-hydroxyethyl ether) ($HOCH_2CH_2OCH_2CH_2OH$). Diethylene glycol is made commercially from either ethylene oxide or ethylene glycol. It is a water-white, odorless and very hygroscopic liquid. It is soluble in water, miscible with many organic solvents, and a solvent for nitrocellulose, shellac, rosin, resins and oils.

Its properties are very much like those of ethylene glycol, but its greater miscibility with certain products gives it a wider range of solvent applications. Diethylene glycol is used as a solvent for dyes in textiles and printing, as a coupling agent in soluble oils, and as an antifreeze. Being highly hygroscopic it is utilized in removing moisture from natural gas, moistening and softening cigarette tobacco, composition cork, casein, gelatin, glues, and paper. It is used as a solvent for dyes used in non grain-raising wood stains and in the manufacture of alkyd resins.

Apparent ignition temperature in air	351°C (663°F)
Boiling point	244.5°C
Coefficient of expansion per °C at 20°C	0.000635
at 55°C	0.000650
Electrical conductivity	0.586×10^{-6} recip. ohms
Flash point (ASTM open cup)	141°C (285°F)
Freezing point	−6.5°C
Heat of vaporization	150 cal./g. at B.P.
Specific gravity at 20/20°C	1.1185
Refractive index at 20°C	1.4475
Specific heat at 20°C	0.5509
Surface Tension at 25°C	48.5 dynes/cm
Viscosity at15°C	0.50 poise
20	0.38 poise
25	0.30 poise
Vapor pressure at 20°C	0.015 mm
Weight per gallon at 20°C	9.308 lbs.
Acidity (as acetic)	0.02% by wt. (max.)
Distillation range at 760 mm	
Below 230°C	None
Below 240	Not over 20%
Below 250	Not less than 85%
Below 270	Not less than 95%
Water	0.30% by wt. (max.)

Dipropylene Glycol ($CH_3CHOHCH_2OCH_2CHOHCH_3$). Dipropylene glycol is a more active solvent than propylene glycol and will dissolve nitrocellulose and rosin. It will partially dissolve cellulose acetate and is soluble to some extent in hydrocarbons (toluene, but not gasoline). It has slight dissolving action in raw linseed oil, shellac and kauri gum; it dissolves some warm vinyl resins, but not dewaxed dammar, ester gum, and unvulcanized rubber. It is less hydroscopic than propylene glycol, and is comparable to diethylene glycol in its industrial applications.

Boiling point	231.8°C
Flash point	280°F
Specific gravity at 20/20°C	1.020–1.030
Vapor pressure at 20°C	0.03 mm
Weight per gallon at 20°C	8.53 lbs.
Acidity (as acetic)	0.01 % by wt. (max.)
Distillation range at 760 mm	215–240°C
Water content	0.5% by wt. (max.)

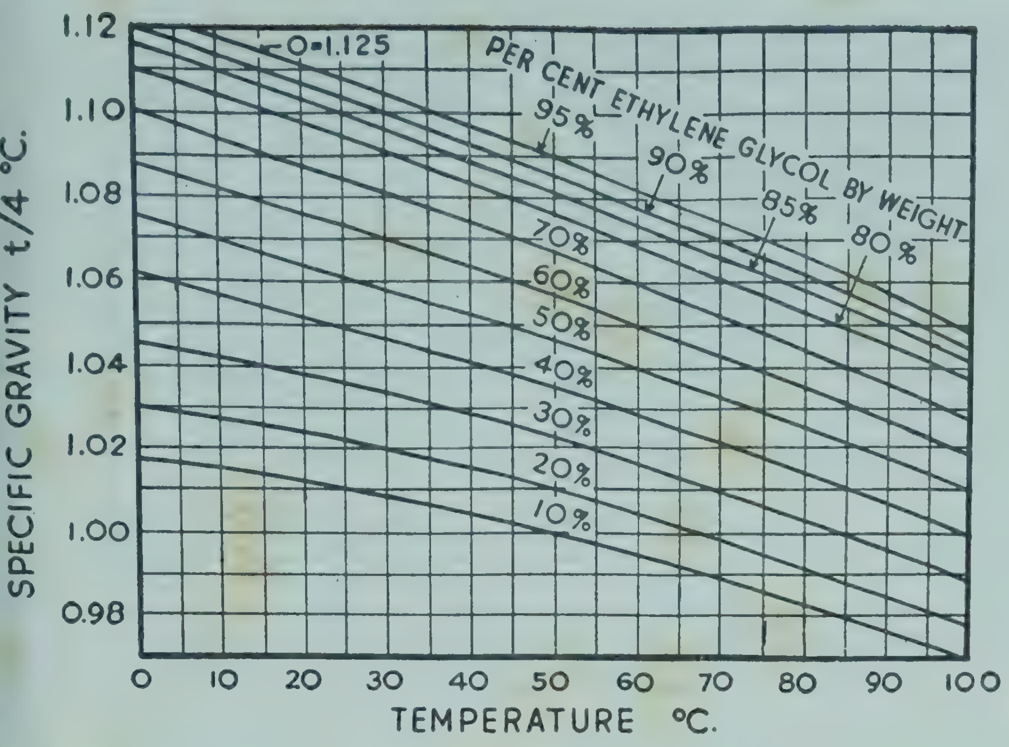


FIGURE 11.67. Specific Gravity of Aqueous Ethylene Glycol Solutions at Various Temperatures.[6]

(Specific Gravity t/4°C. × 1.0018 = Specific Gravity t/20°C.)

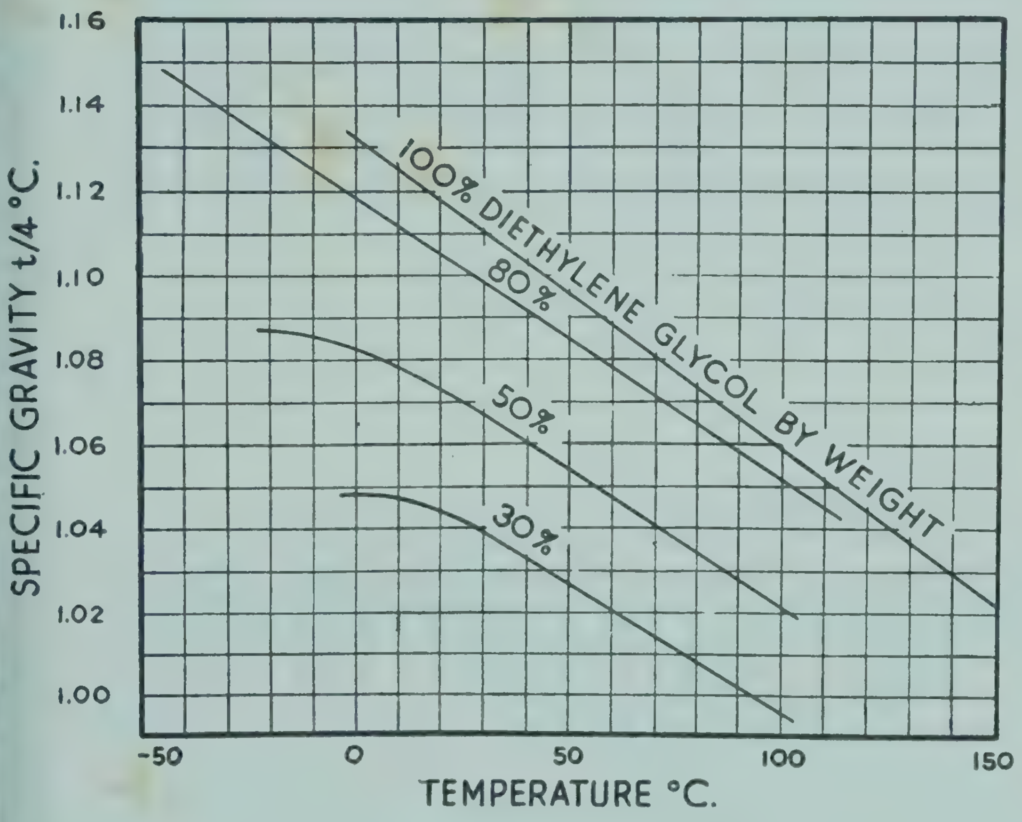


FIGURE 11.68. Specific Gravity of Aqueous Diethylene Glycol Solutions at Various Temperatures.[6]

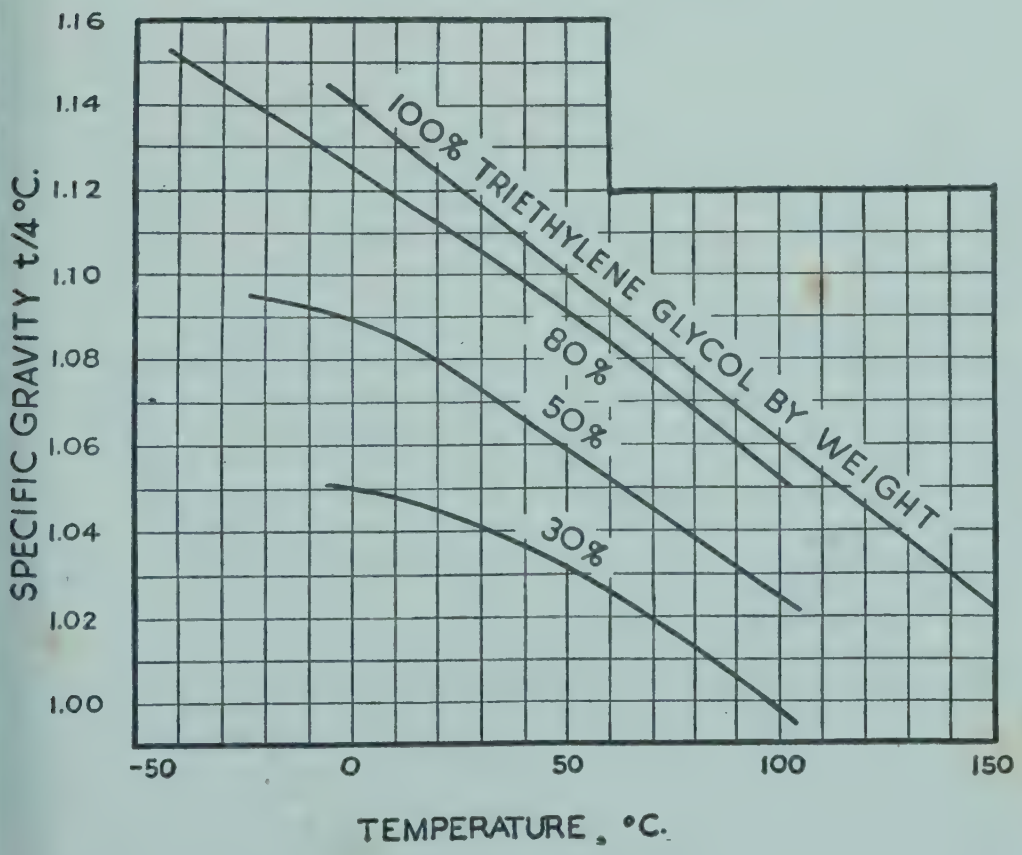


FIGURE 11.69. Specific Gravity of Aqueous Triethylene Glycol Solutions at Various Temperatures.[6]

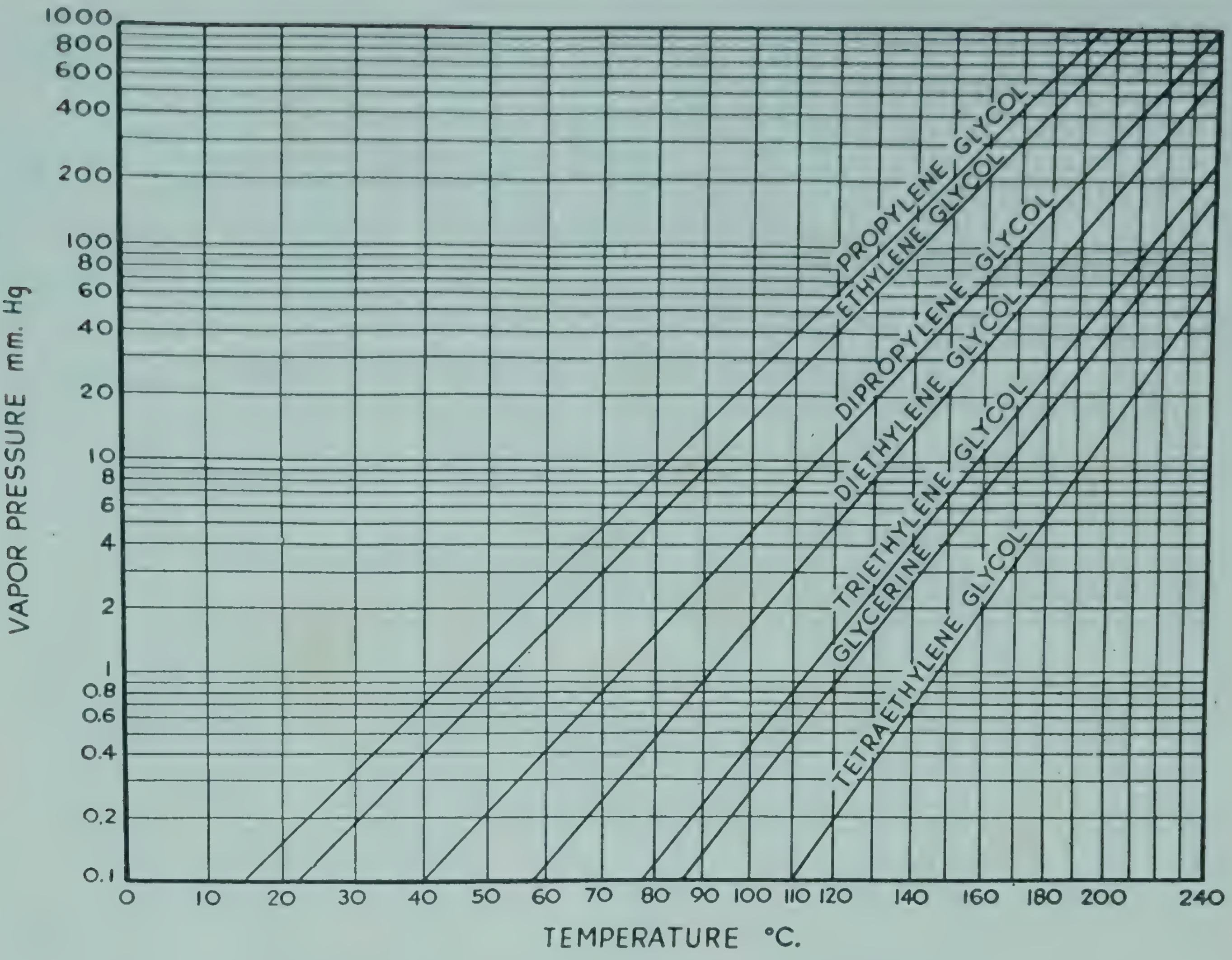


Figure 11.70. Vapor Pressures of Glycols.[6]

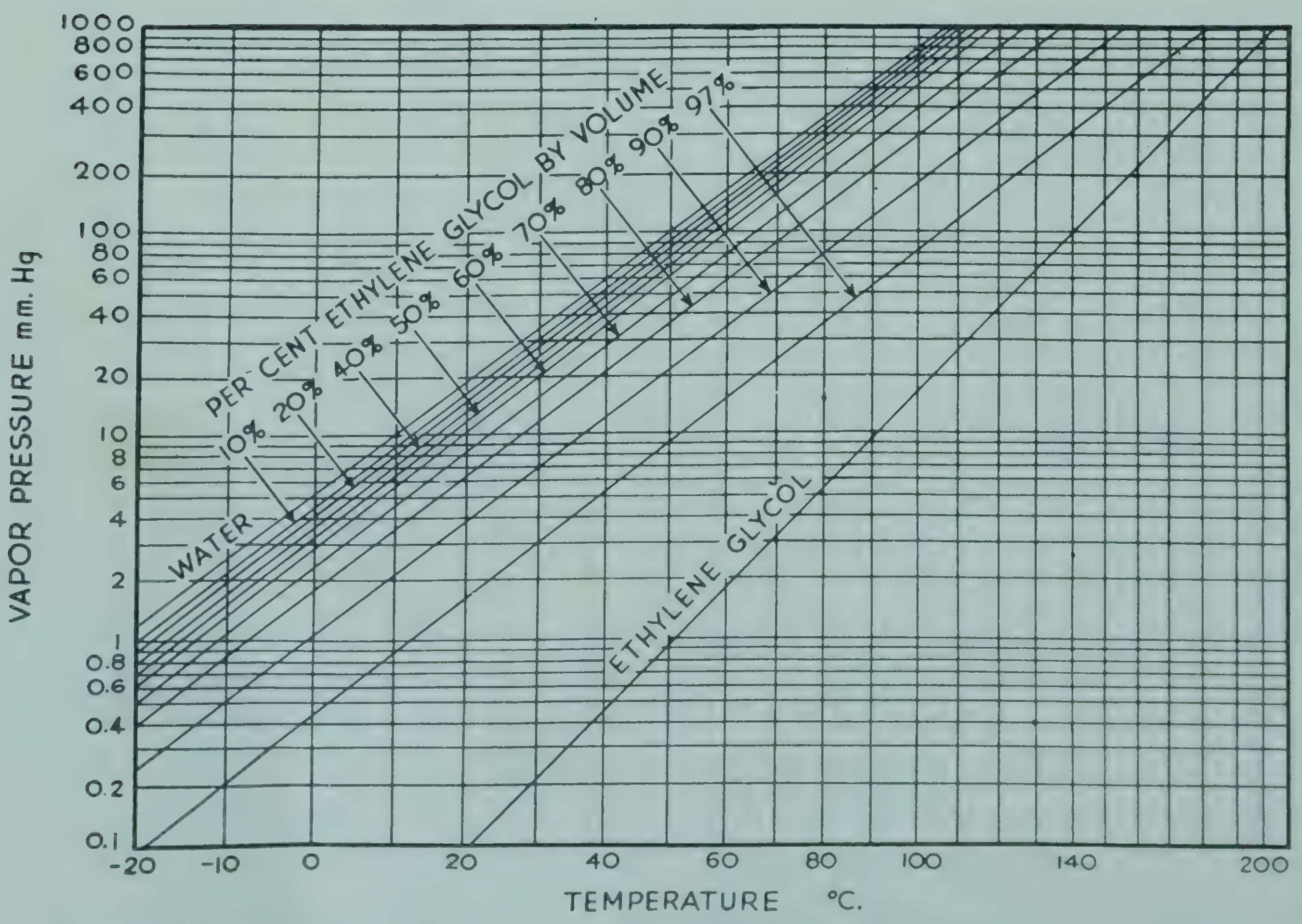


Figure 11.71. Vapor Pressure of Aqueous Ethylene Glycol Solutions.[6]

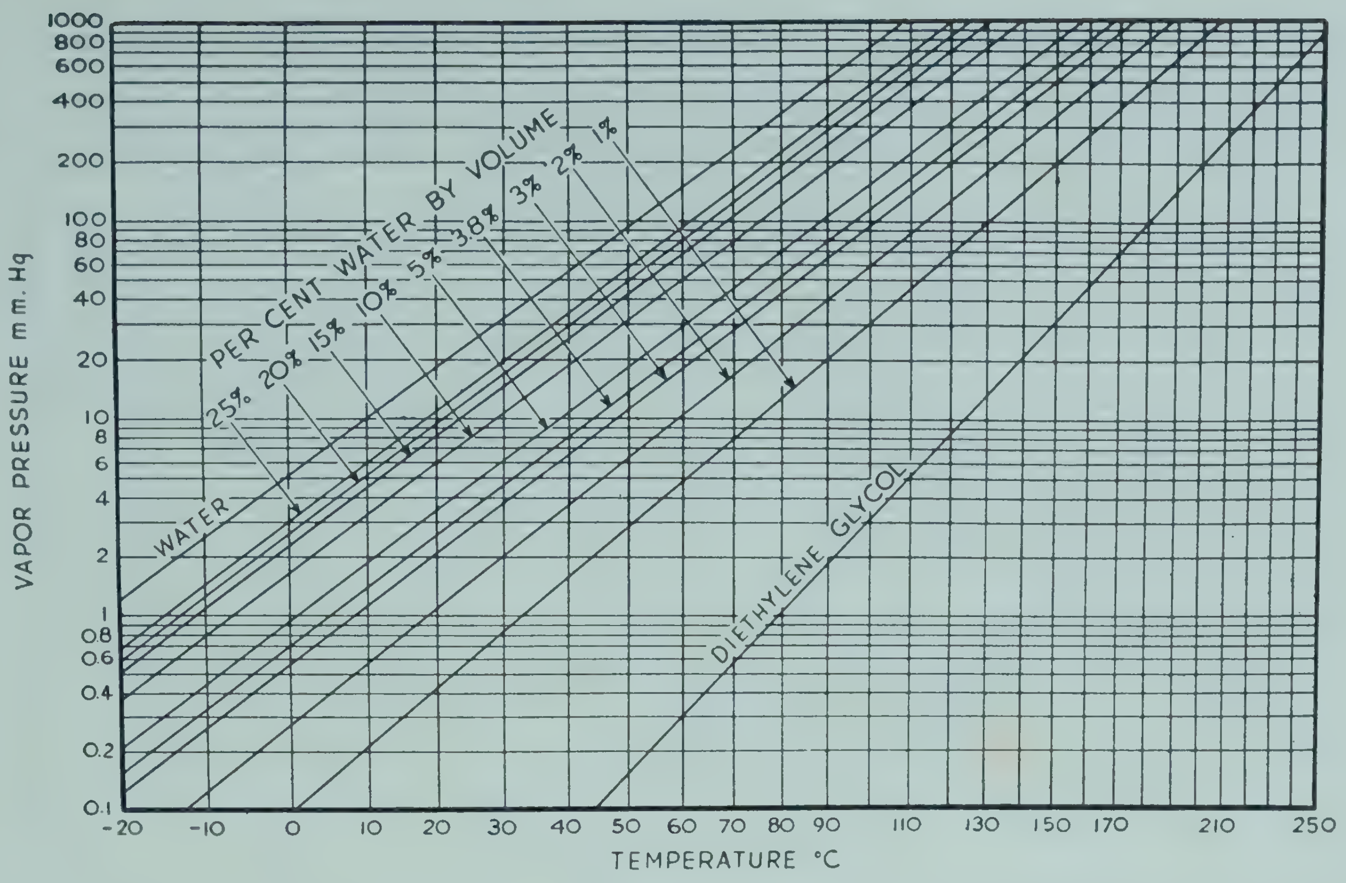


Figure 11.72. Vapor Pressure of Aqueous Diethylene Glycol Solutions[6]

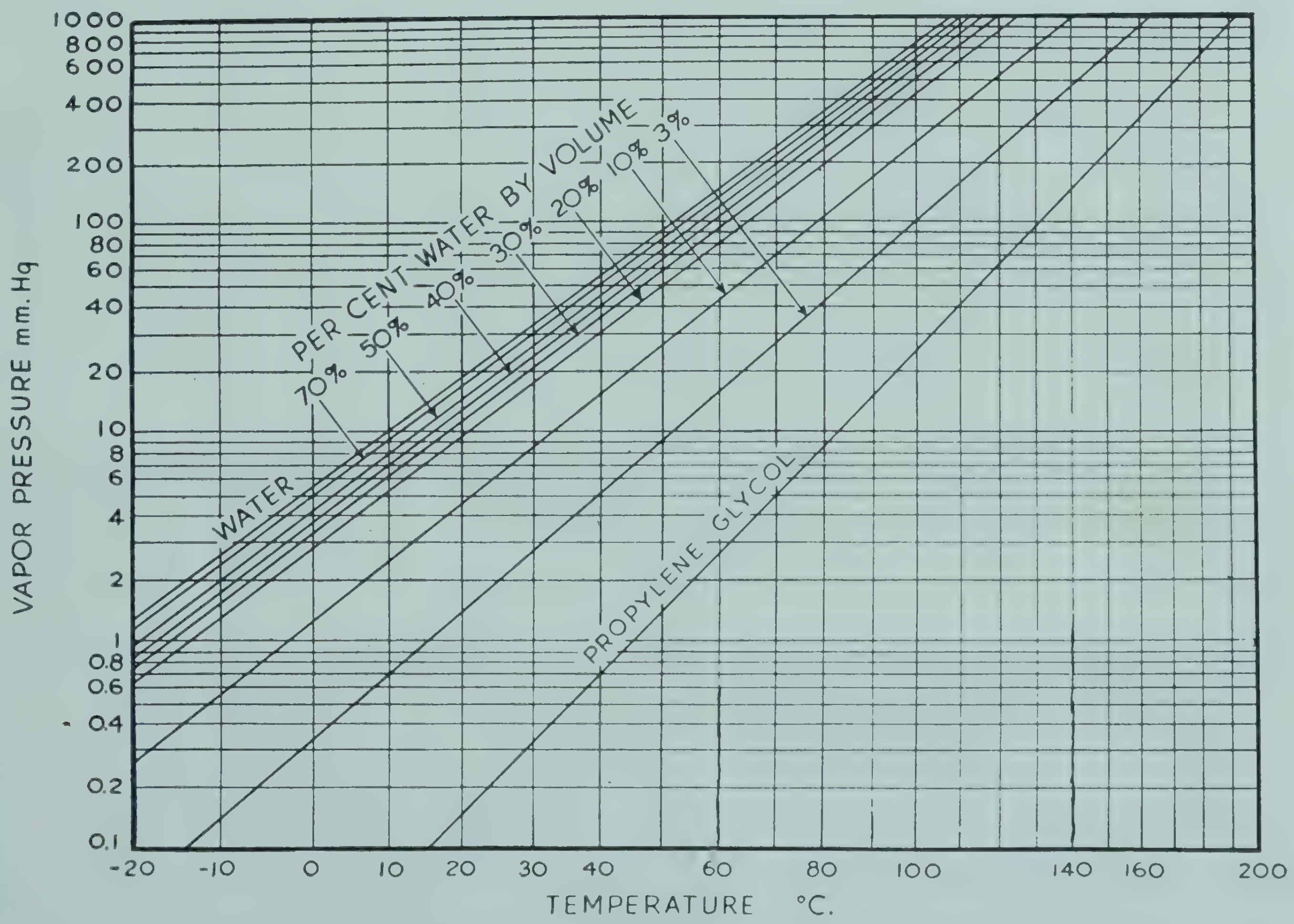


Figure 11.73. Vapor Pressure of Aqueous Propylene Glycol Solutions.[6]

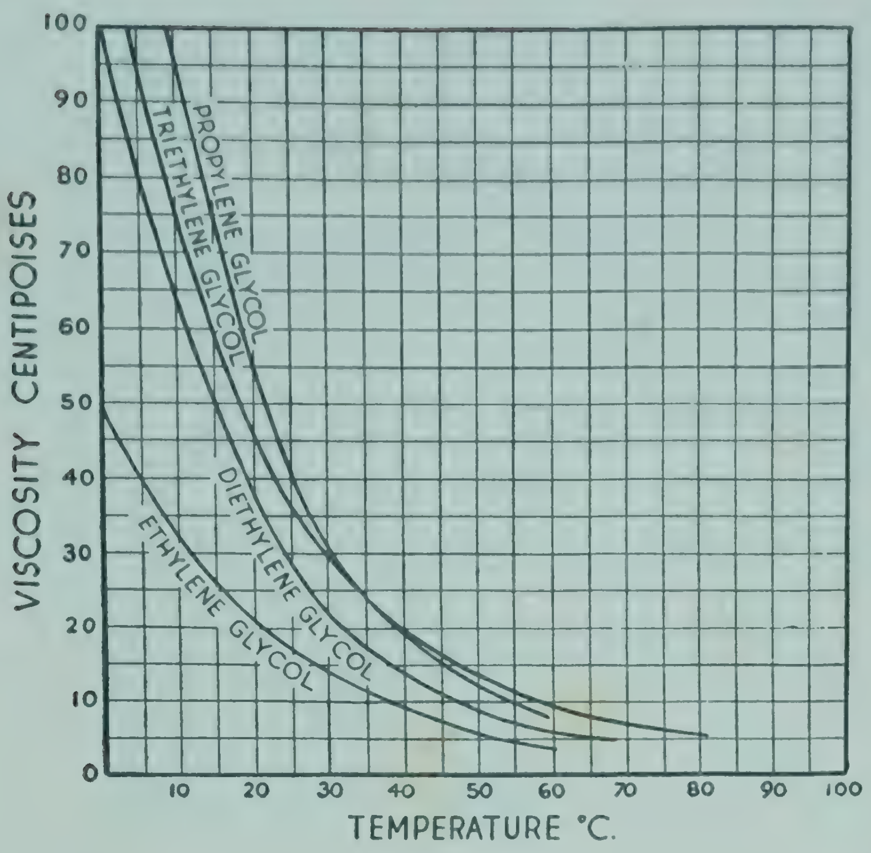


Figure 11.74. Viscosity at Various Temperatures.[6]

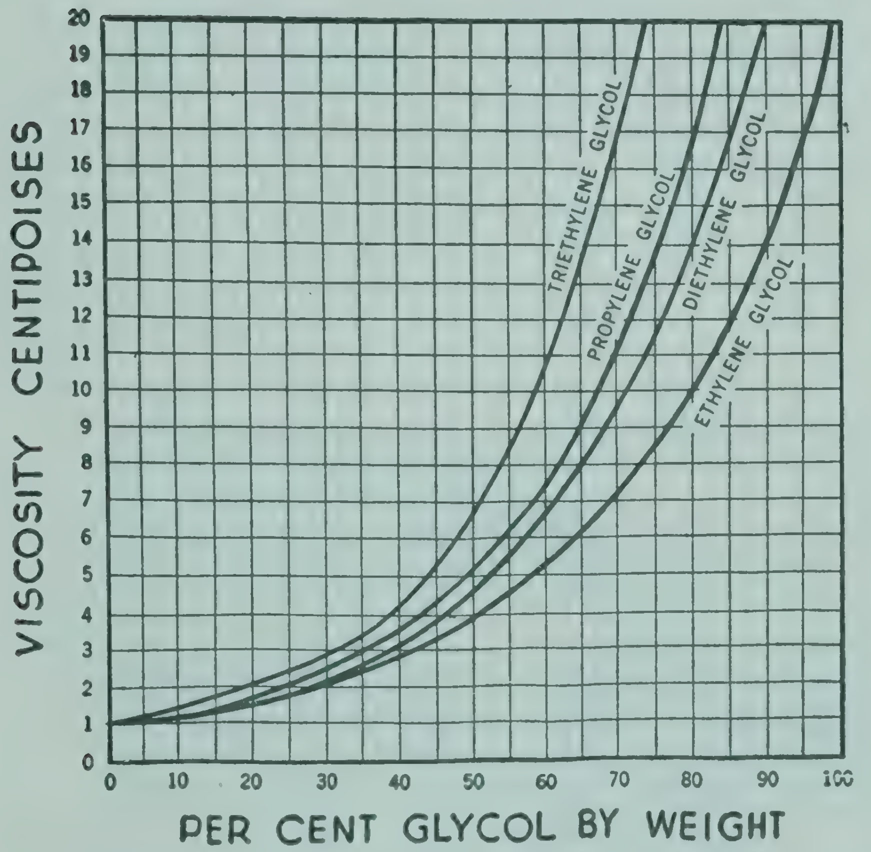


Figure 11.75. Viscosity of Aqueous Solutions at 20°C.[6]

Trimethylene Glycol (1,3-Propandiol) ($HOCH_2CH_2CH_2OH$). Trimethylene glycol, a by-product of soap manufacture, is an oily liquid, soluble in water and alcohol. Like propylene glycol it may be used as an antifreeze, and in alkyd resin manufacture.

Boiling point	214°C
Specific gravity at 20/4°C	1.060

Triethylene Glycol (Triglycol, Hydroxyethoxyethoxyethanol) ($HOCH_2 \cdot CH_2OCH_2CH_2HOC_2CH_2OH$). Triethylene glycol is a stable, high-boiling water-white, hygroscopic liquid. It is freely soluble in water and alcohol, very slightly soluble in ethyl ether and insoluble in benzene, toluene and

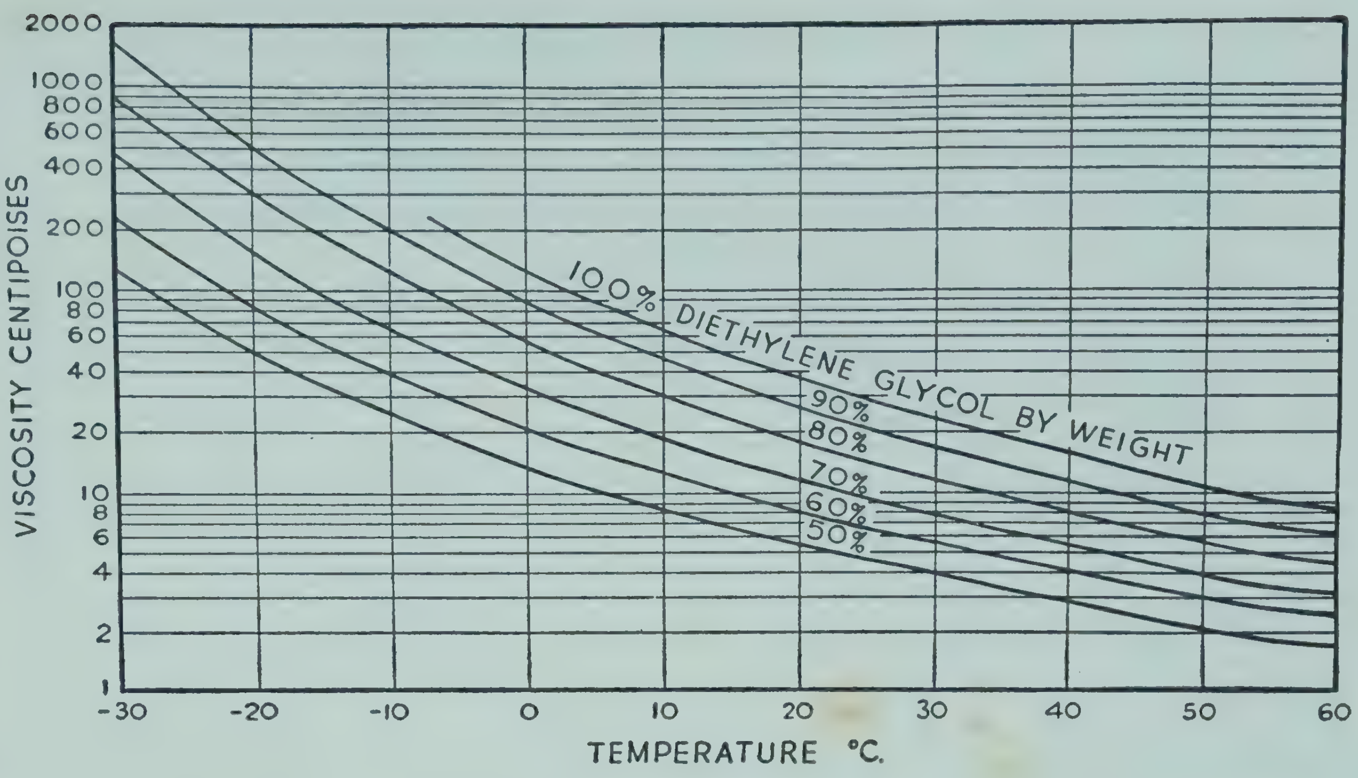


FIGURE 11.76. Viscosity of Aqueous Diethylene Glycol Solutions at Various Temperatures.[6]

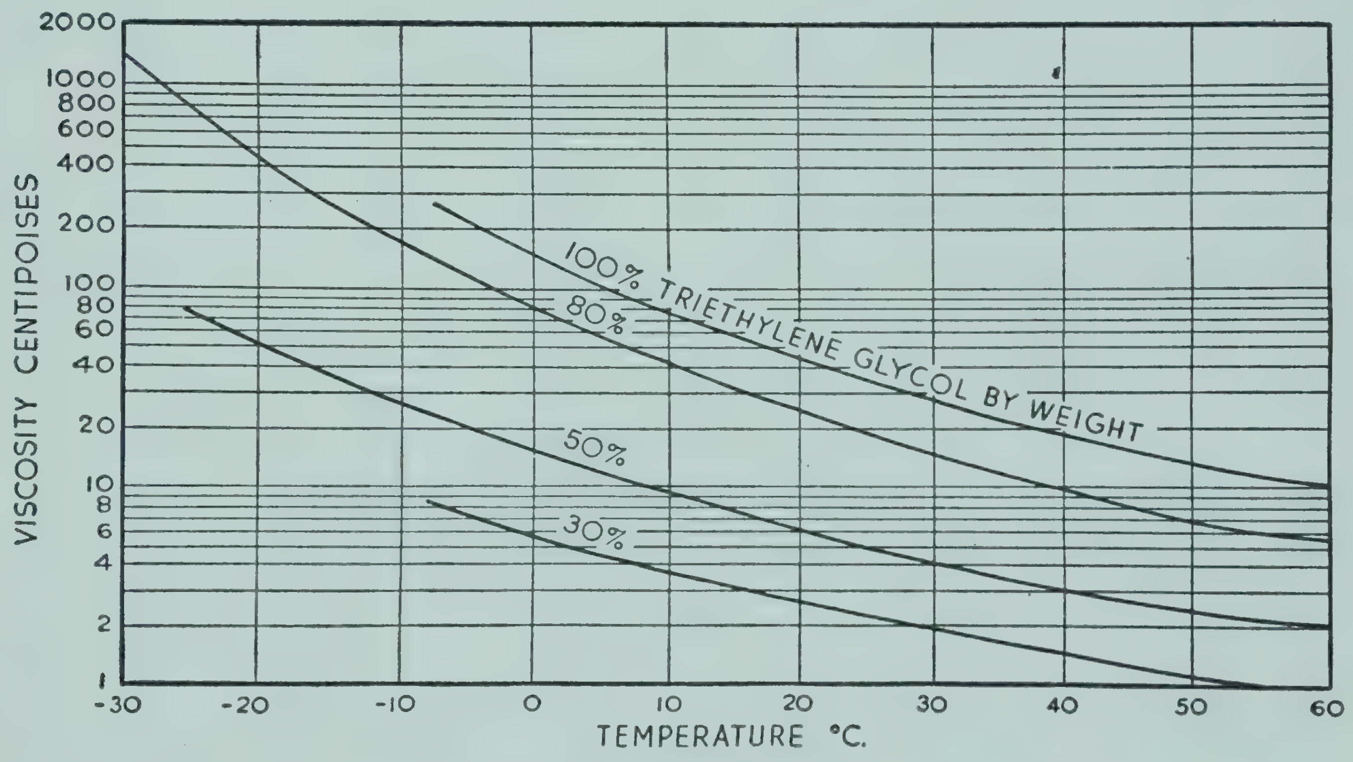


FIGURE 11.77. Viscosity of Aqueous Triethylene Glycol Solutions at Various Temperatures.[6]

gasoline. It has two hydroxyl groups as well as two ether groups, making it a good solvent for nitrocellulose and natural and synthetic gums and resins. Its uses are similar to those of diethylene glycol since their properties are much alike. Important applications include its use as a high-temperature heat transfer medium, a dehydrating and sterilizing agent in air-conditioning equipment and manufacture of synthetic resins. Its esters are important plasticizers for vinyl and other synthetic resins.

Typical Properties and Specifications

Boiling point	287.3°C
Distillation range at 760 mm	270–300°C
Coefficient of expansion per °C	0.00071 up to 55°C
Flash Point (ASTM open cup)	166°C
Freezing point	−7.2°C
Specific gravity at 20/20°C	1.1254
Refractive index at 20°C	1.4559
Specific heat at 28 to 33°C	0.528
Surface tension at 20°C	45.24 dynes/cm
Vapor pressure at 20°C	0.0004 mm
Viscosity at 20°C	0.478 poise
Weight per gallon at 20°C	9.365 lbs.
Acidity (as acetic)	0.02% by wt. (max.)

Polyethylene Glycols [$HO(CH_2 \cdot CH_2O)xH$]. These glycols are colorless, hygroscopic and somewhat viscous liquids, with low vapor pressures. They are less hygroscopic than the lower glycols and are freely soluble in water and aromatic hydrocarbons, but are insoluble in aliphatic hydrocarbons. Polyethylene glycol 200 is mainly composed of tetraethylene glycol; polyethylene glycol 300 of hexaethylene glycol; and polyethylene glycol 400 of octaethylene glycol. The polyethylene glycols are solvents for nitrocellulose and are used as plasticizers for gelatin and casein products, cork, glues and in steam-set printing inks. They are also used in the manufacture of wetting agents, emulsifiers, detergents, and alkyd resins.

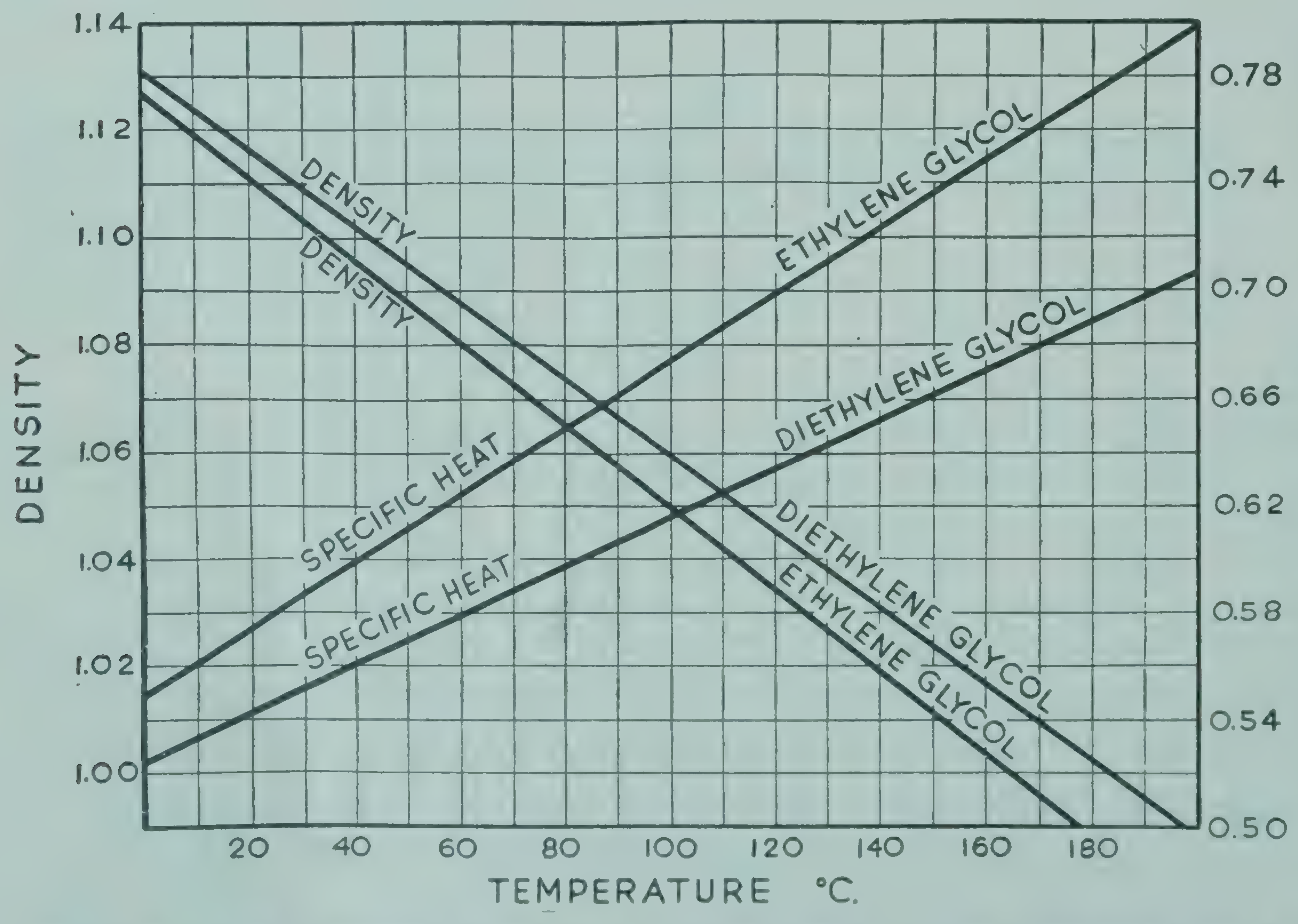


FIGURE 11.78. Specific Heat and Density at Various Temperatures.[6]

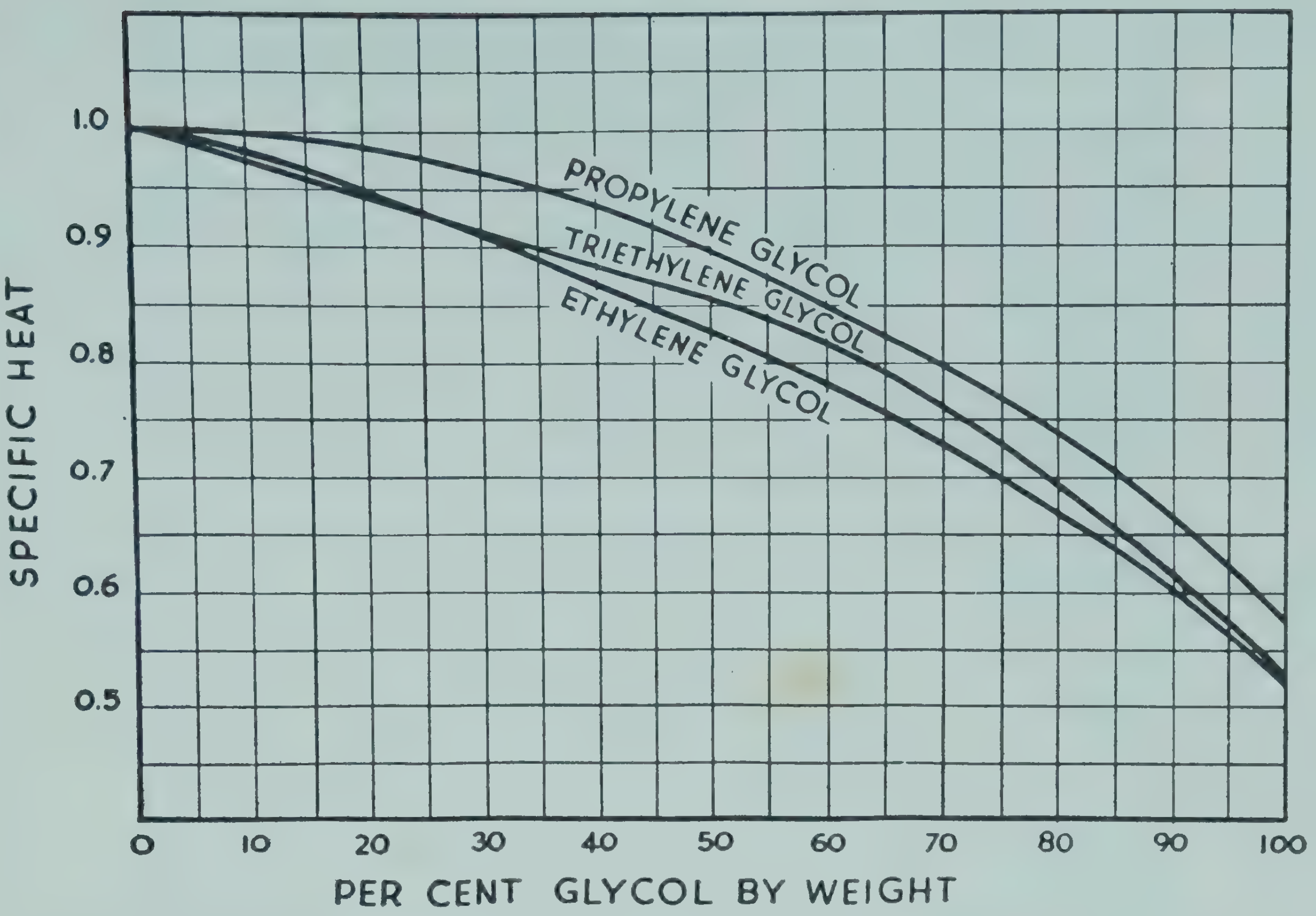


FIGURE 11.79. Specific Heat of Aqueous Solutions at 28 to 33°C.[6]

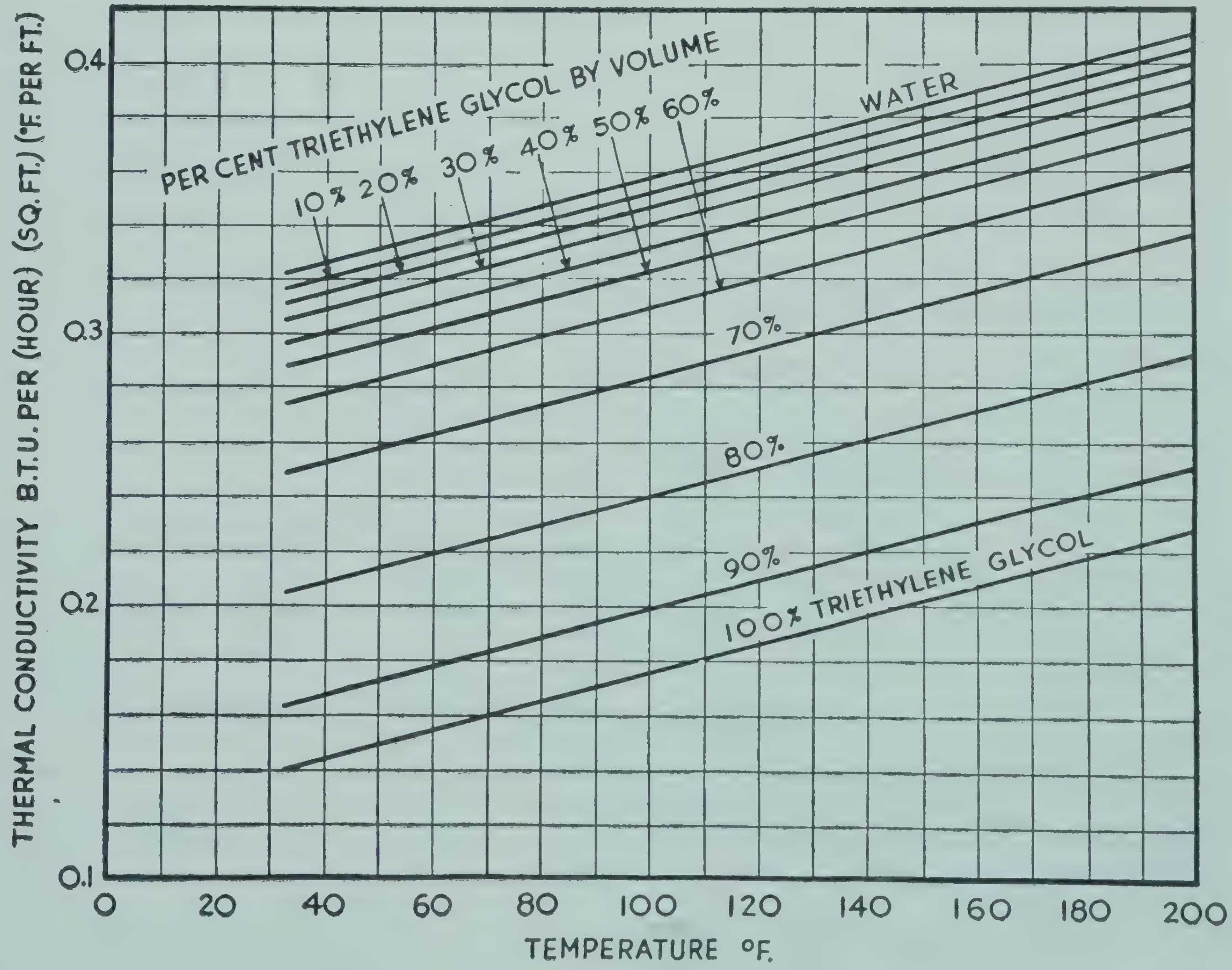


FIGURE 11.80. Thermal Conductivity (Calculated) of Aqueous Triethylene Glycol Solutions at Various Temperatures.[6]

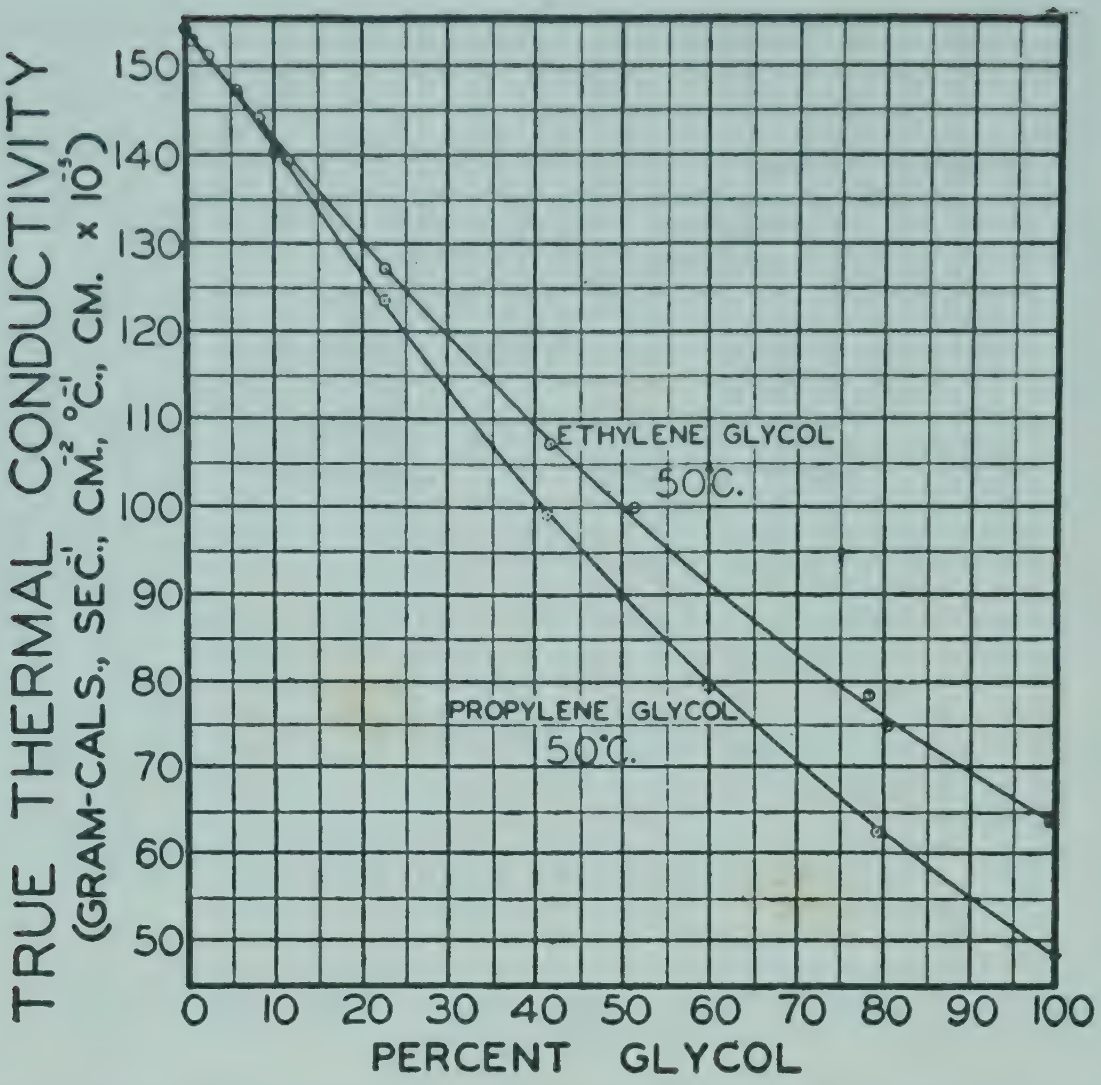


Figure 11.81. Variation in Thermal Conductivity with Composition of Glycol-Water Mixtures.[19]

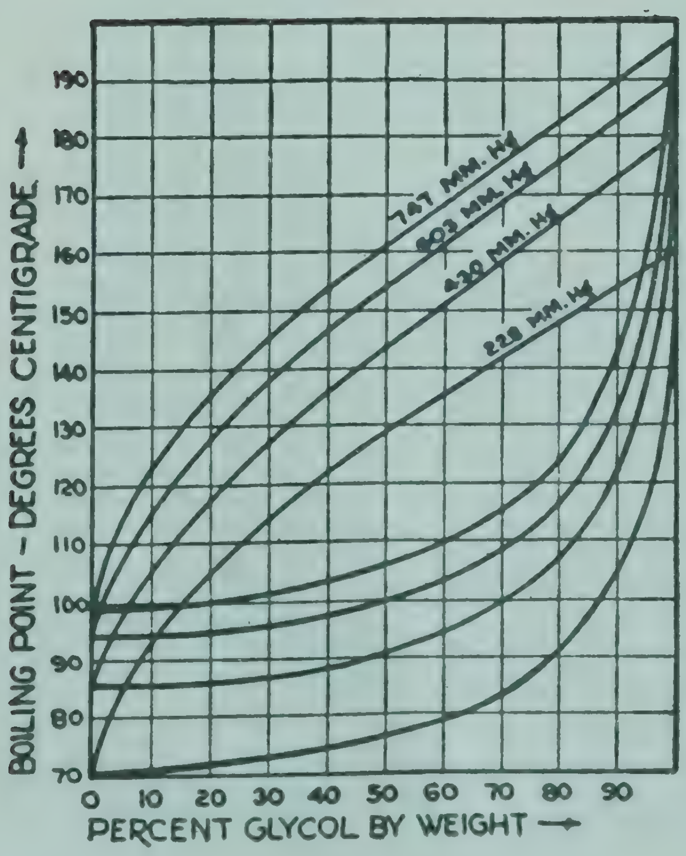


Figure 11.82. Boiling Points of Glycol-Water Mixtures.[20]

Upper curves: vapor composition vs. boiling point.

Lower curves: liquid composition vs. boiling point.

Physical Properties

	Liquid Polyethylene Glycols 200	300	400	600
Average Molecular Weight	190 to 210	285 to 315	380 to 420	570 to 630
Freezing Range °C	Supercools	−15 to 8	4 to 10	20 to 25
Specific Gravity 20/20°C	1.12	1.13	1.13	1.13
Flash Point, °F	350	385	435	475
Saybolt Viscosity at 210°F sec.	38 to 41	42 to 46	45 to 55	60 to 70
Water Solubility at 20°C % by weight	Complete	Complete	Complete	Complete
Comparative Hygroscopicity (Glycerol = 100)	90	70	60	50

(a) Density, g. per cc. at 20°C.

Compatibilities

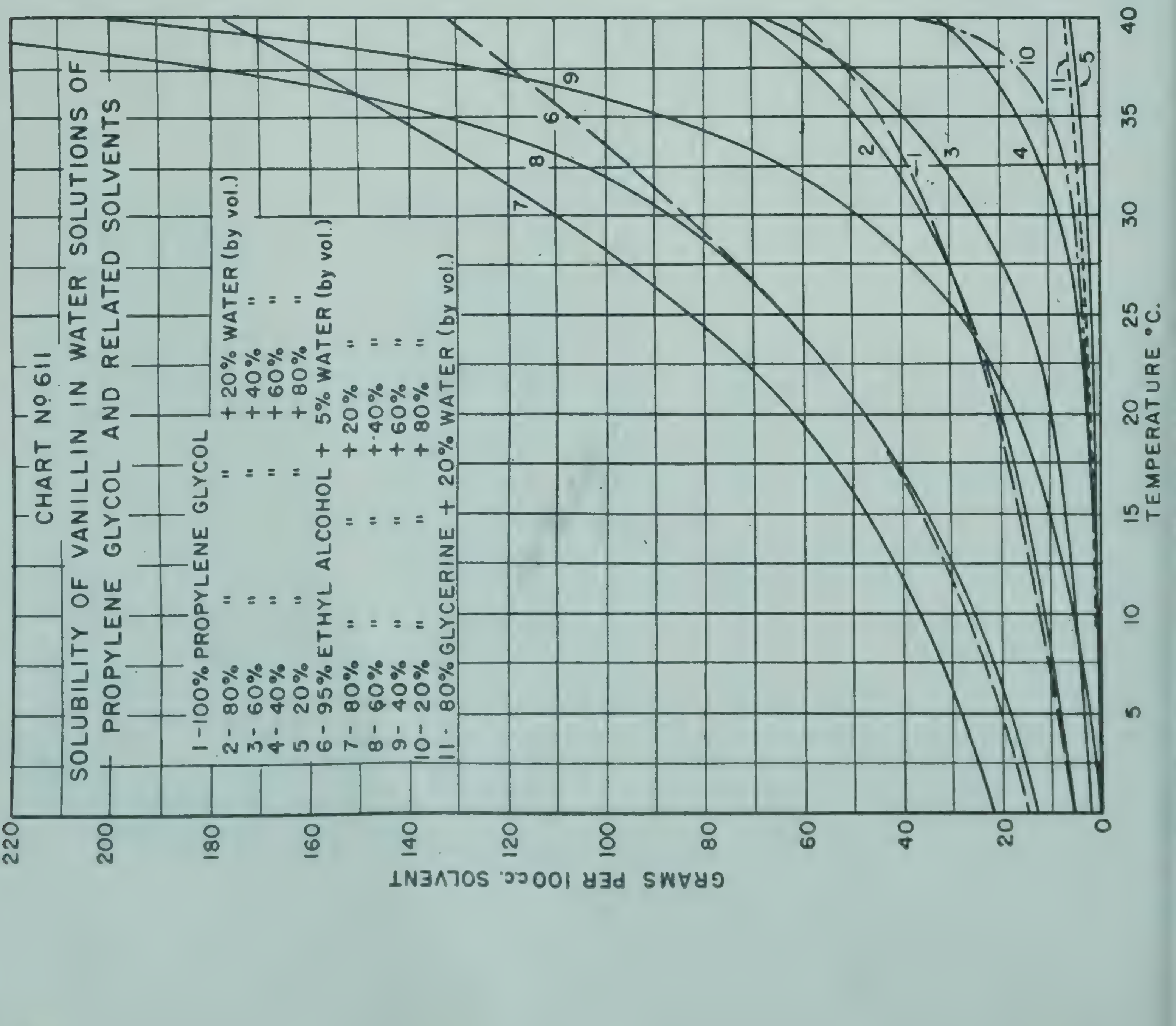
	Polyethylene Glycol 400
Nitrocellulose	C
Ethyl Cellulose	I
Methyl Cellulose	PC
"Bakelite" BR3360	C
"Bakelite" BR8900	C
"Vinylite" AYAF	C
Shellac	PC
Carnauba Wax (No. 3)	I
Paraffin Wax	I
Beeswax	I
Ester Gum	I
Rosin	C
Gum Arabic	I
Raw Castor Oil	I
Tung Oil	I
Mineral Oil	I
Olive Oil	I
Pine Oil	C
Casein	C
Zein	C
Chlorinated Starch	C
Gelatin	I

C = Compatible or Soluble
PC = Partly Compatible
I = Incompatible.

Solubilities

	Approximate per cent by weight Polyethylene Glycol 400 20°C	50°C
Water	C	C
Methanol	C	C
Ethanol (200-proof)	C	C
Acetone	C	C
Dichlorethyl Ether	C	C
Trichlorethylene	C	C
"Cellosolve"	C	C
Butyl "Cellosolve"	C	C
"Carbitol"	C	C
Butyl "Carbitol"	C	C
Ethyl Acetate	C	C
Dimethyl Phthalate	C	C
Dibutyl Phthalate	C	C
Ethyl Ether	I	I(a)
Isopropyl Ether	I	I
Toluene	C	C
Heptane	I	I

(a) Insoluble at boiling point
I = Insoluble
C = Greater than 100 g. per 100 cc. of solvent.



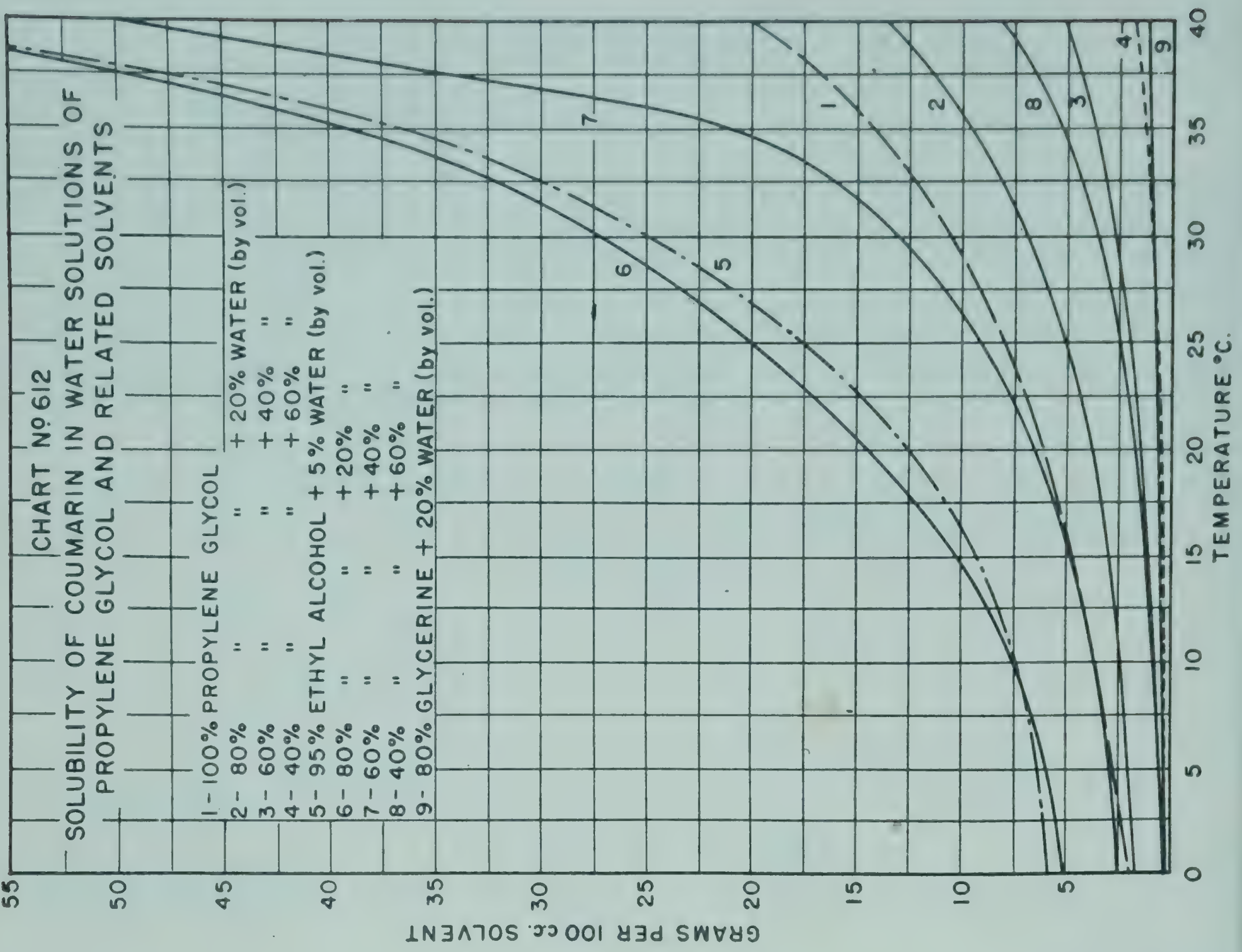


FIGURE 11.84[6]

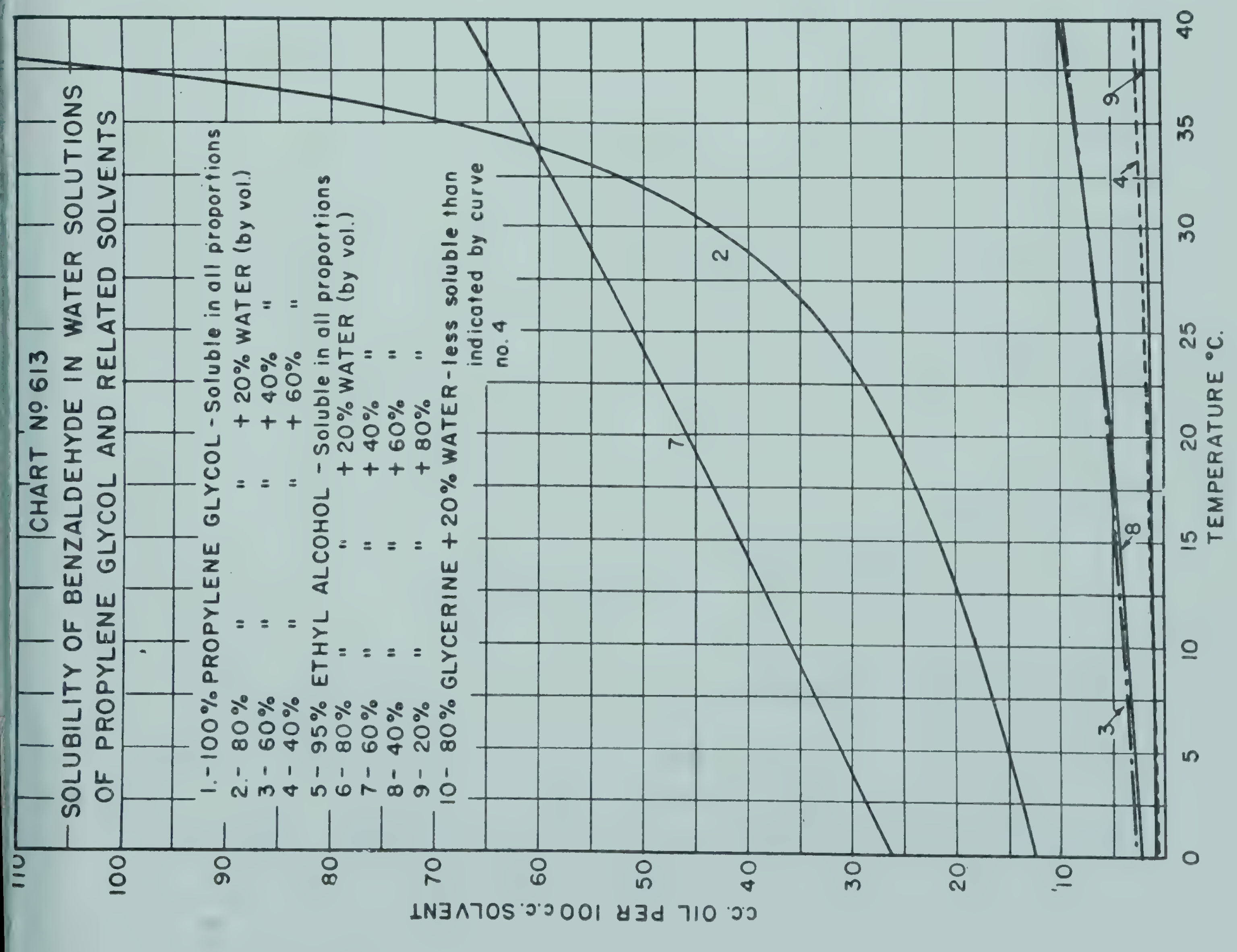


FIGURE 11.85^6

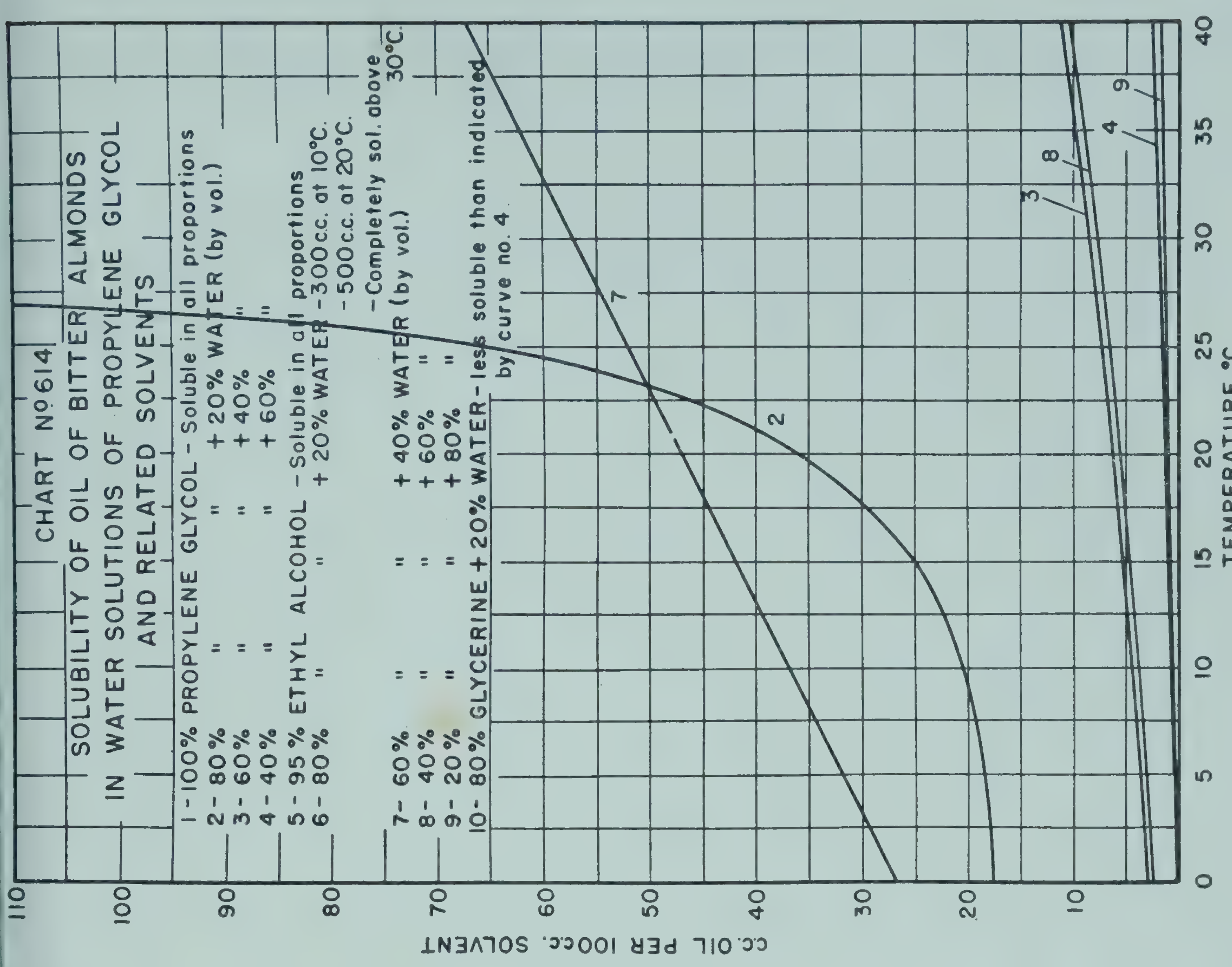


FIGURE 11.86^6

POLYPROPYLENE GLYCOLS

Polypropylene Glycol 150[6]

Polypropylene glycol 150 is a practically colorless, water-soluble, high-boiling liquid having an average molecular weight of approximately 150. It is miscible with many organic solvents including toluene, but not gasoline. It is a solvent for cellulose nitrate, shellac, kauri gum, rosin, castor oil, and castor oil derivatives, but it does not dissolve dammar or ester gum. It is immiscible with soybean oil and olive oil. Low- and high-viscosity cellulose acetate are partially dissolved by this glycol. Its use as a heat-transfer medium is suggested by the fact that polypropylene glycol 150 possesses excellent stability toward oxidation. A 90-hr. laboratory oxidation test with air in glass at 210°F. will increase the initial acidity (as acetic) of 0.04 per cent by weight to only 0.22 per cent by weight.

Polypropylene glycol 150 shows promise as a plasticizer, humectant, and solvent in casein and gelatin compositions, glues, zein, cork, and special printing inks, where advantage may be taken of its low vapor pressure and hygroscopicity. The two alcohol groups contained in the molecule can be esterified with organic acids. Resins of the alkyd type may be formed by reacting polypropylene glycol 150 with dibasic acids to give materials possessing different and unusual properties. When esterified with only one molecule of fatty acid, polypropylene glycol 150 forms excellent emulsifying agents and detergents that are not affected by acids and hard water. Polypropylene glycol 150 and its derivatives tend to be more oil-soluble than corresponding diethylene glycol derivatives.

Physiological action: While polypropylene glycol 150 is of low toxicity it must not be confused with propylene glycol, and it is not considered safe to incorporate in any products intended for internal consumption. The single dose oral toxicity of polypropylene glycol is low but it shows evidence of possible cumulative effects on repeated dosage.

Typical Properties and Specifications

Specific Gravity at 20/20°C	1.0200 to 1.0300
Boiling Range at 760 mm.	Below 200°C not more than 5%
Maximum Acidity, % by wt. as acetic	<0.01
Water Content, % by weight	<0.1
Maximum Color, A.P.H.A. Units	<20

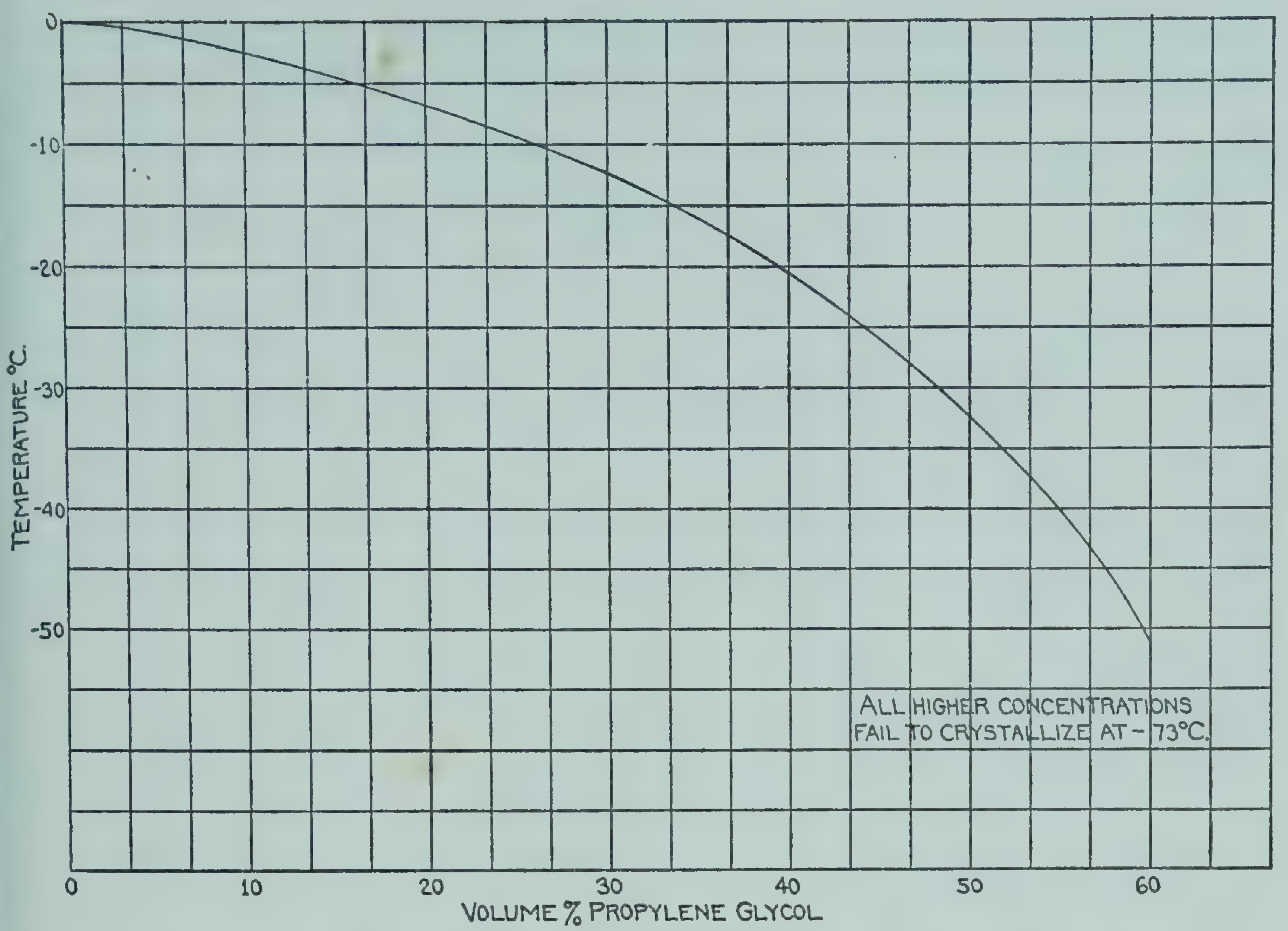


FIGURE 11.87. Freezing Point of Propylene Glycol-Water Mixtures at Various Temperatures.[6]

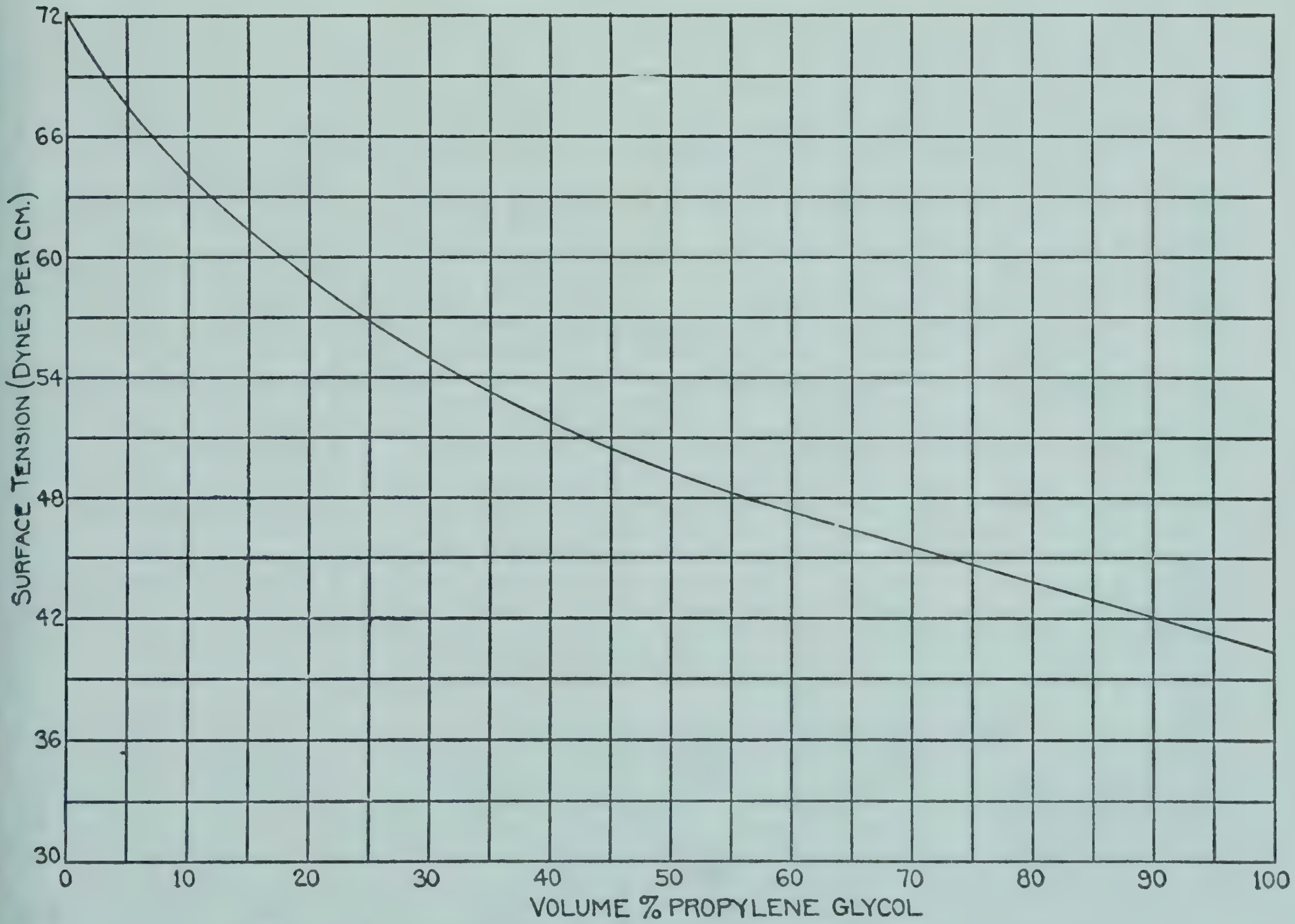


FIGURE 11.88. Surface Tension of Propylene Glycol-Water Mixtures at 25° C. (Approx.).[6]

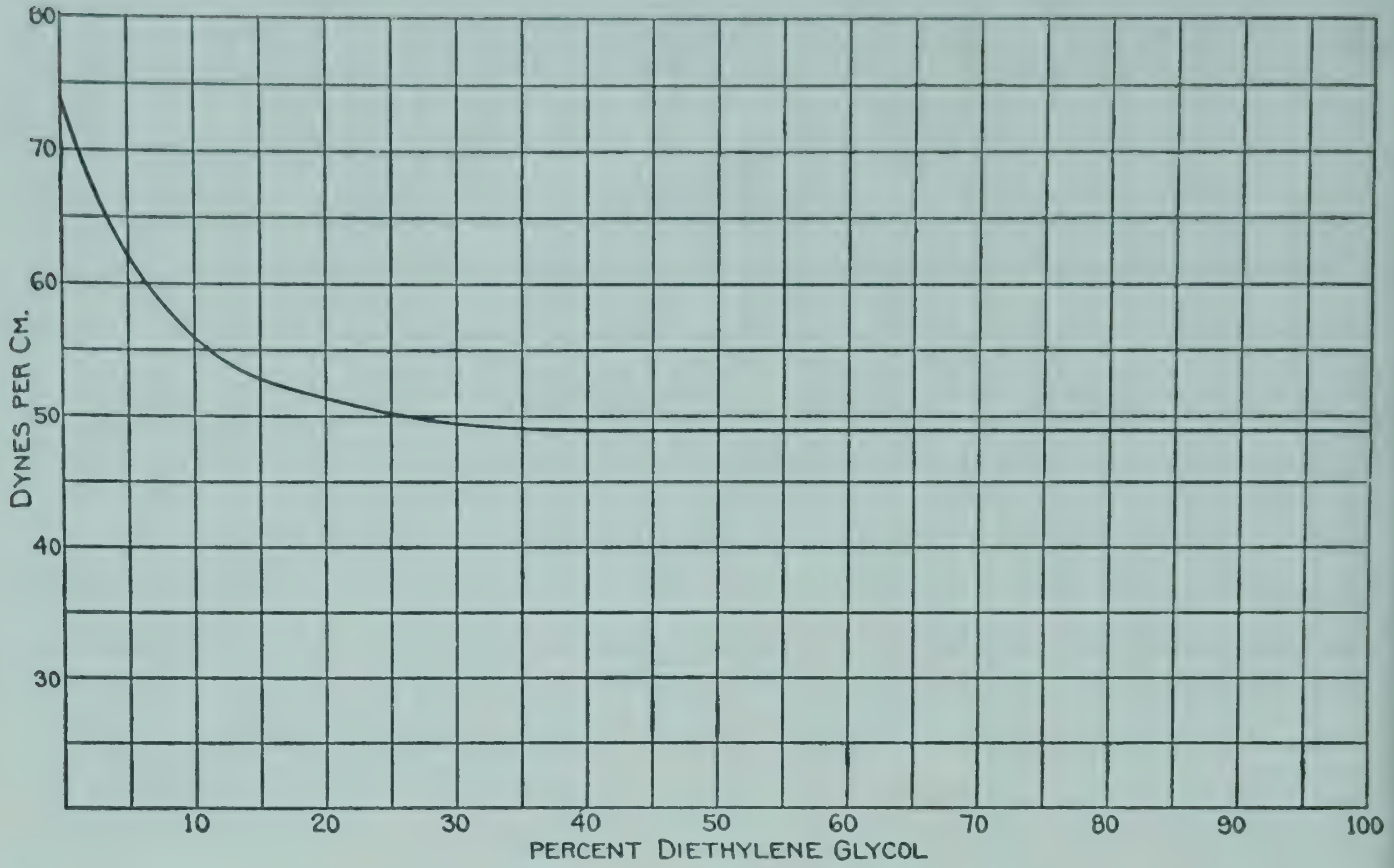


FIGURE 11.89. Surface Tension of Diethylene Glycol-Water Mixtures.[6] (du Noüy Apparatus. Water = 74 dynes,sq. cm.)

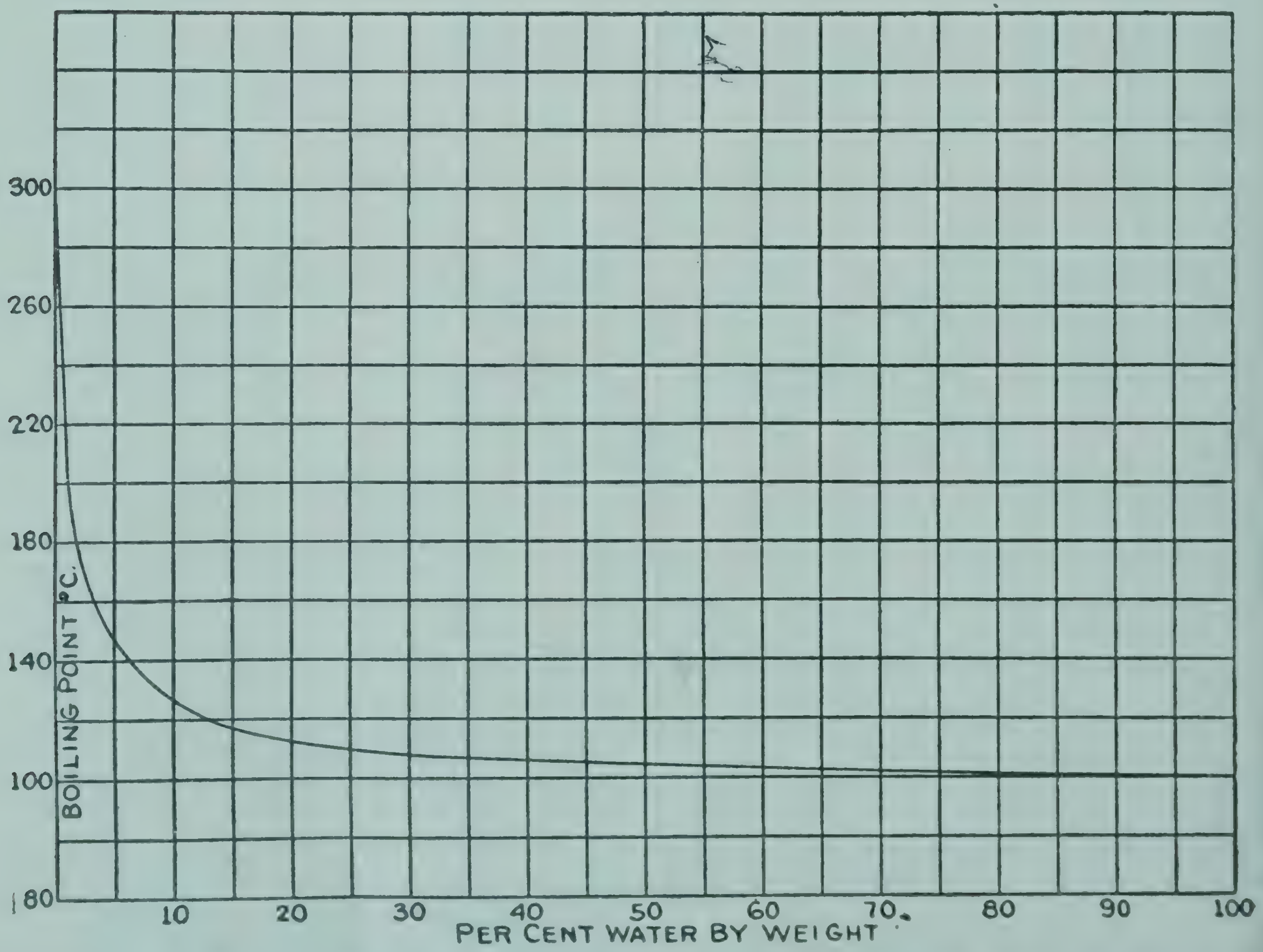


FIGURE 11.90. Boiling Point Curves for Aqueous Triethylene Glycol Solutions.[6]

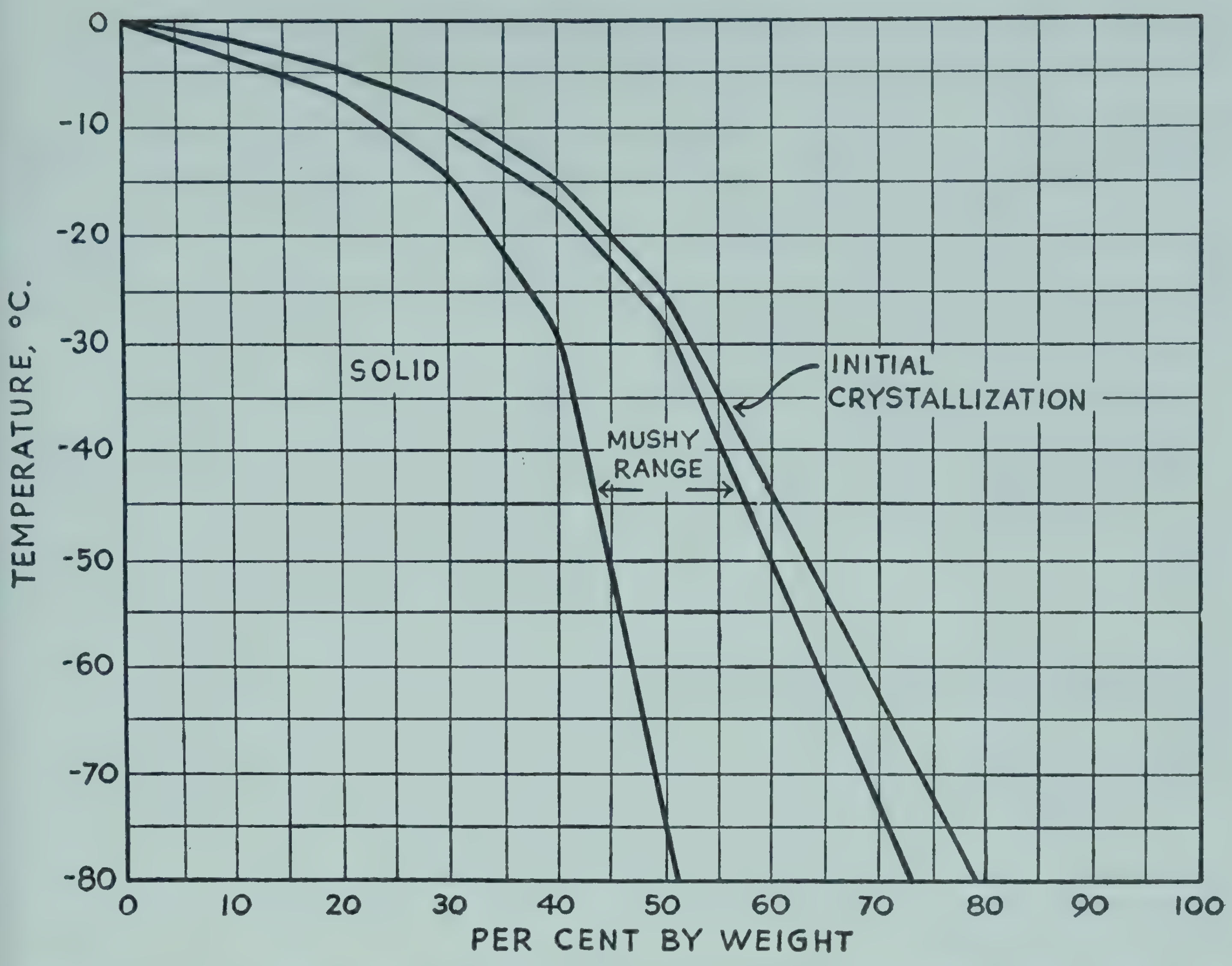


FIGURE 11.91. Approximate Freezing Point Curves for Aqueous Triethylene Glycol Solutions.[6]

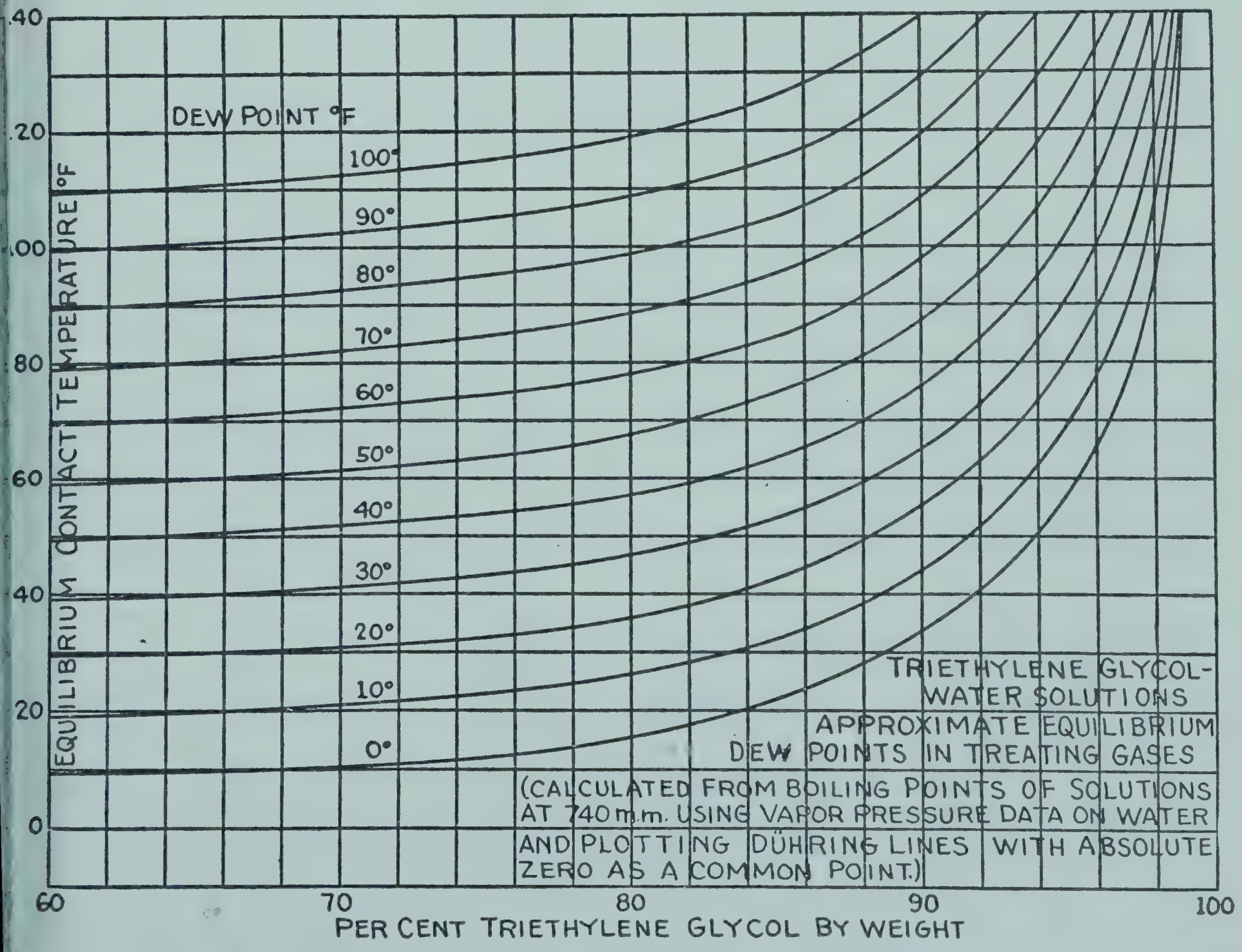


FIGURE 11.92. Triethylene Glycol Aqueous Solutions Equilibrium Dew Points In Treating Gases.[3]

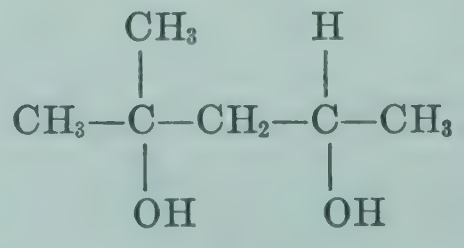
Polypropylene Glycols of 400, 750 and 1200 Average Molecular Weights[18]

	P-400	P-750	P-1200
Properties:			
Specific gravity at 25/25°C	1.007	1.004	1.003
at 75/20°C	0.967	0.965	0.965
Pour point (ASTM) °C	−39	−40	−34
Flash point (ASTM) °C	207	240	246
Fire point (ASTM) °C	224	263	290
Surface tension:			
Dynes per cm. at 25°C	32	32	31
Dynes per cm. at 75°C	28	28	28
Viscosity at 25°C, centipoises	67	96	144
at 75°C, centipoises	8	12	18
Color	Colorless to light straw	Colorless to light straw	Colorless to light straw
Solubility, grams per 100 grams solvent			
Acetone at 25°C	∞	∞	∞
Benzene at 25°C	∞	∞	∞
Carbon tetrachloride at 25°C	∞	∞	∞
Ether at 25°C	∞	∞	∞
Methanol at 25°C	∞	∞	∞
n-Heptane at 25°C	∞	∞	∞
Cyclohexane at 25°C	∞	∞	∞
Ethanol (Formula 30) at 25°C	∞	∞	∞
Monochlorobenzene at 25°C	∞	∞	∞
Water at 25°C	∞	30	<0.1
Water at 75°C	<0.1	<0.1	<0.1
Solubility of water in POLYGLYCOL, grams per 100 grams POLYGLYCOL			
At 25°C	∞	<0.1	<0.1
At 75°C	31	<0.1	<0.1

Handling Precautions: Preliminary toxicological investigations indicate that these materials present no unusual health hazards and that no special precautions are necessary for safe handling. Prolonged and repeated contact on the skin should be avoided because there may be a slight absorption from such exposures.

Safe Uses: These materials are suitable for all uses that do not lead to appreciable oral ingestion or to extensive skin contact. They should not be incorporated into foods or into any product that is to be taken internally or to be applied extensively to the skin until it has been demonstrated that such uses are entirely safe.

2-Methyl-2,4-Pentanediol (hexylene glycol)



$$CH_3-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-\underset{\underset{OH}{|}}{\overset{\overset{H}{|}}{C}}-CH_3$$

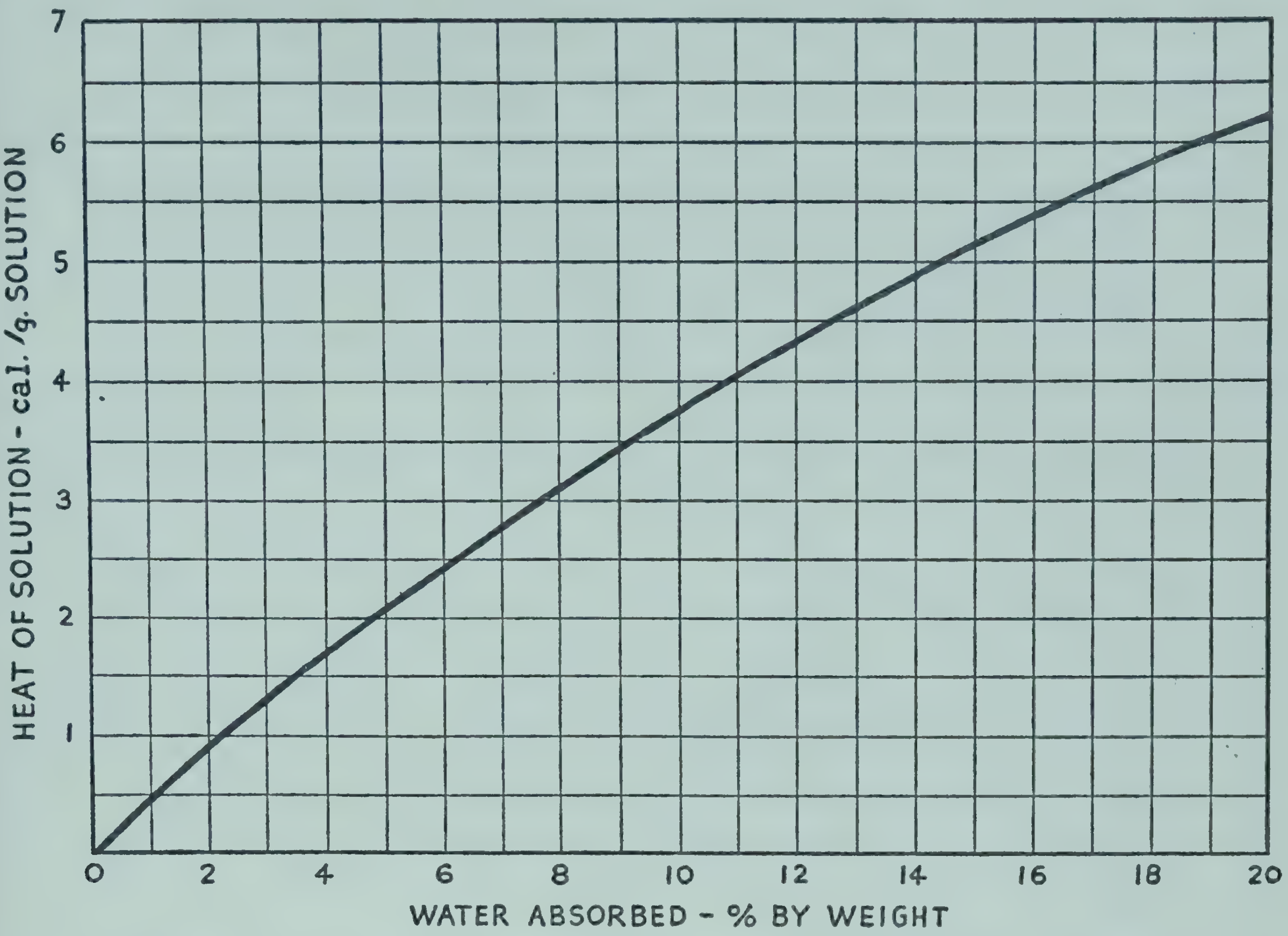


FIGURE 11.93. Heat of Solution of Water in Triethylene Glycol.[6]

Methylpentanediol is a colorless, hygroscopic and high-boiling liquid. This dihydric alcohol is miscible with a large number of organic solvents, as shown below. It is used as a mutual solvent, a humectant, as a brake fluid diluent, as a softening agent, cement grinding aid and solvent in steam-set printing inks.

Boiling point	198.5°C
Flash point (Cleveland Open Cup)	200°F
Heat of Vaporization	12,900 Cal./mole
Pour point	−35°F
Refractive index, 20/D	1.4274
Specific gravity 20°/4°C	0.922
Vapor pressure	

t° C	P in mm	t° C	P in mm
20	0.02	160	214.4
90	7.68	170	306.5
100	13.83	180	429.0
110	23.83	190	588.8
120	39.43	198.5	760
130	62.96	200	793.8
140	97.38	210	1053
150	146.4		

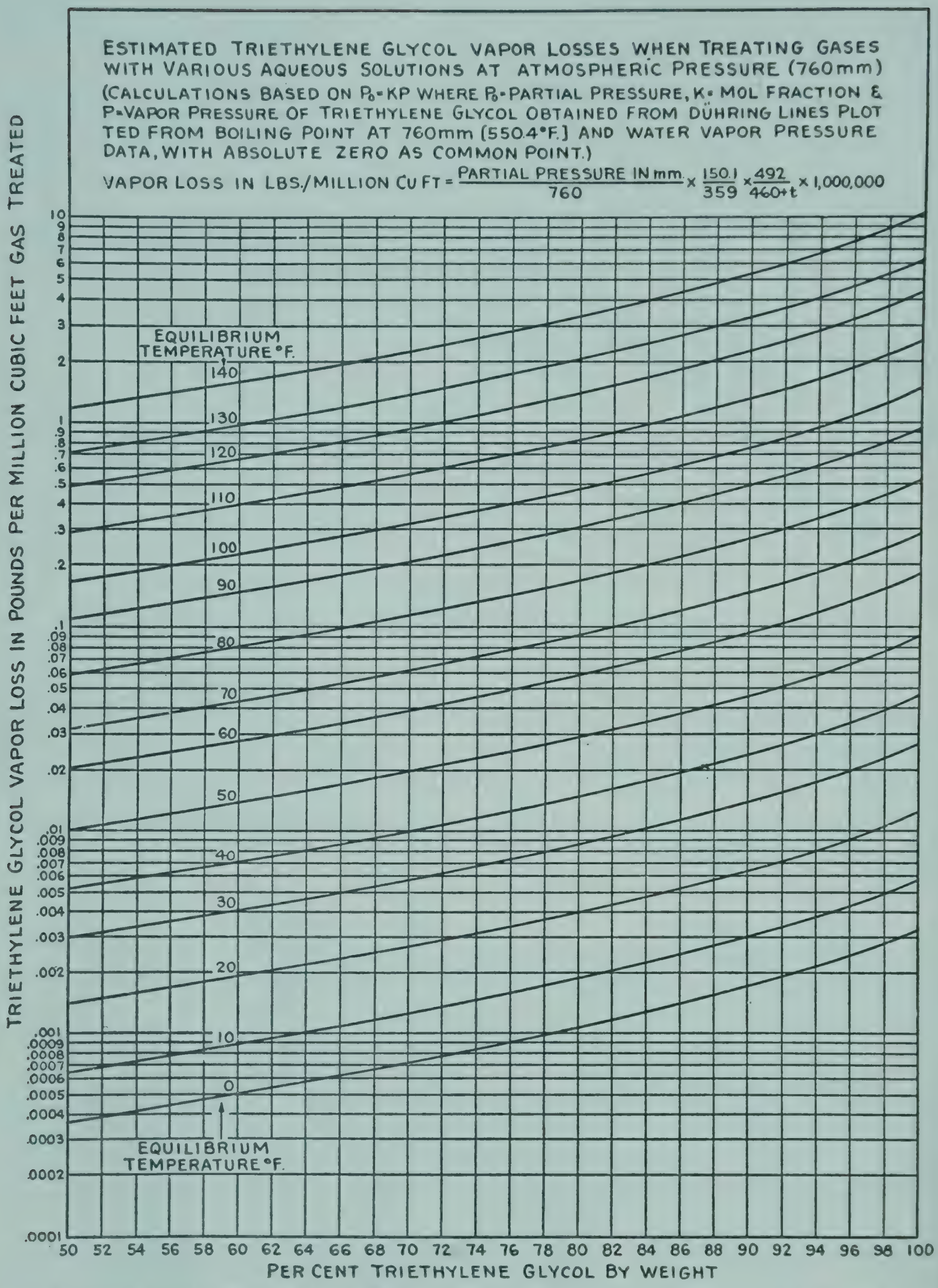


FIGURE 11.94. Triethylene Glycol Vapor Losses when Treating Gases.[6]

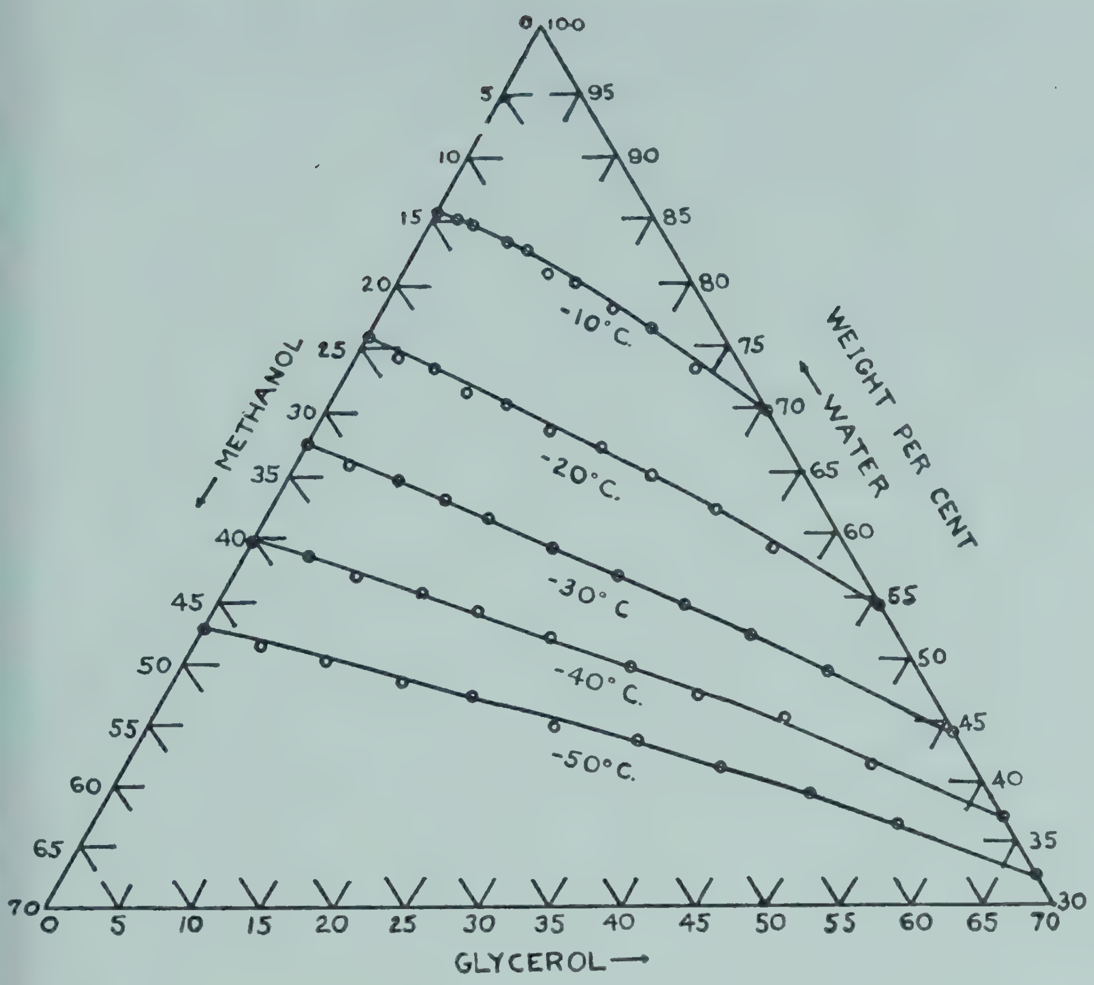


FIGURE 11.95 Freezing Point of Aqueous Glycerol-Methanol Solutions.[25]

Vicosity

Temperature (°F)	Viscosity (centistokes)
−30	18,860
−15	4,580
0	1,355
32	189.(9)
68	41.(8)
100	15.9(8)
210	2.20(6)

Weight per gallon at 20°C	7.69 lbs. (approx.)
Acidity (as acetic)	0.01% by wt. (max.)
Distillation range	192°–200°C

Substances with which Methylpentamediol is Miscible[5]

- Water
- Ketones
  - Acetone
  - Methyl ethyl ketone
  - Diacetone
  - Methyl isobutyl ketone
  - Mesityl oxide
- Chlorides
  - Ethylene dichloride
  - Trichloroethylene
  - Carbon tetrachloride
  - 1,2,3-Trichloropropane
- Alcohols
  - Ethyl
  - Isopropyl
  - *sec.*-Butyl
  - *n*-Butyl
  - Methylamyl
- Hydrocarbons
  - Mineral spirits
  - Petroleum ether
  - Stoddard solvent
  - Octanes
  - Toluene

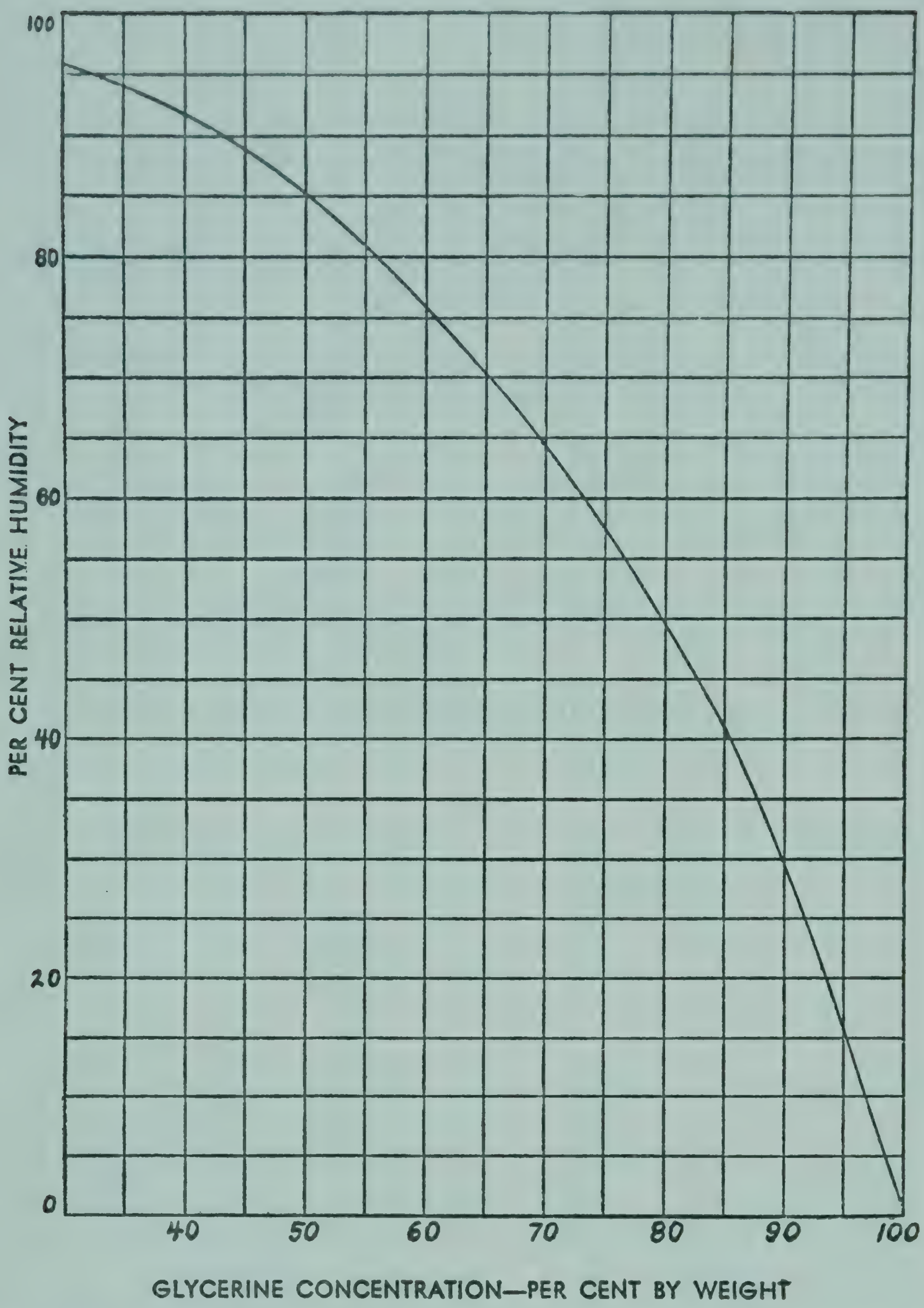


FIGURE 11.96. Relative Humidity over Aqueous Glycerine Solutions.[22] 15–45°C.

- Ethers
  - Ethyl ether
  - Isopropyl ether
- Acids
  - Acetic
  - Oleic
  - Phosphoric
- Esters
  - *n*-Butyl acetate
  - Ethyl acetate
- Plasticizers
  - Dibutyl phthalate
  - Dibutyl sebacate
  - Castor oil
- Amines
  - Cyclohexylamine
  - Triethanolamine

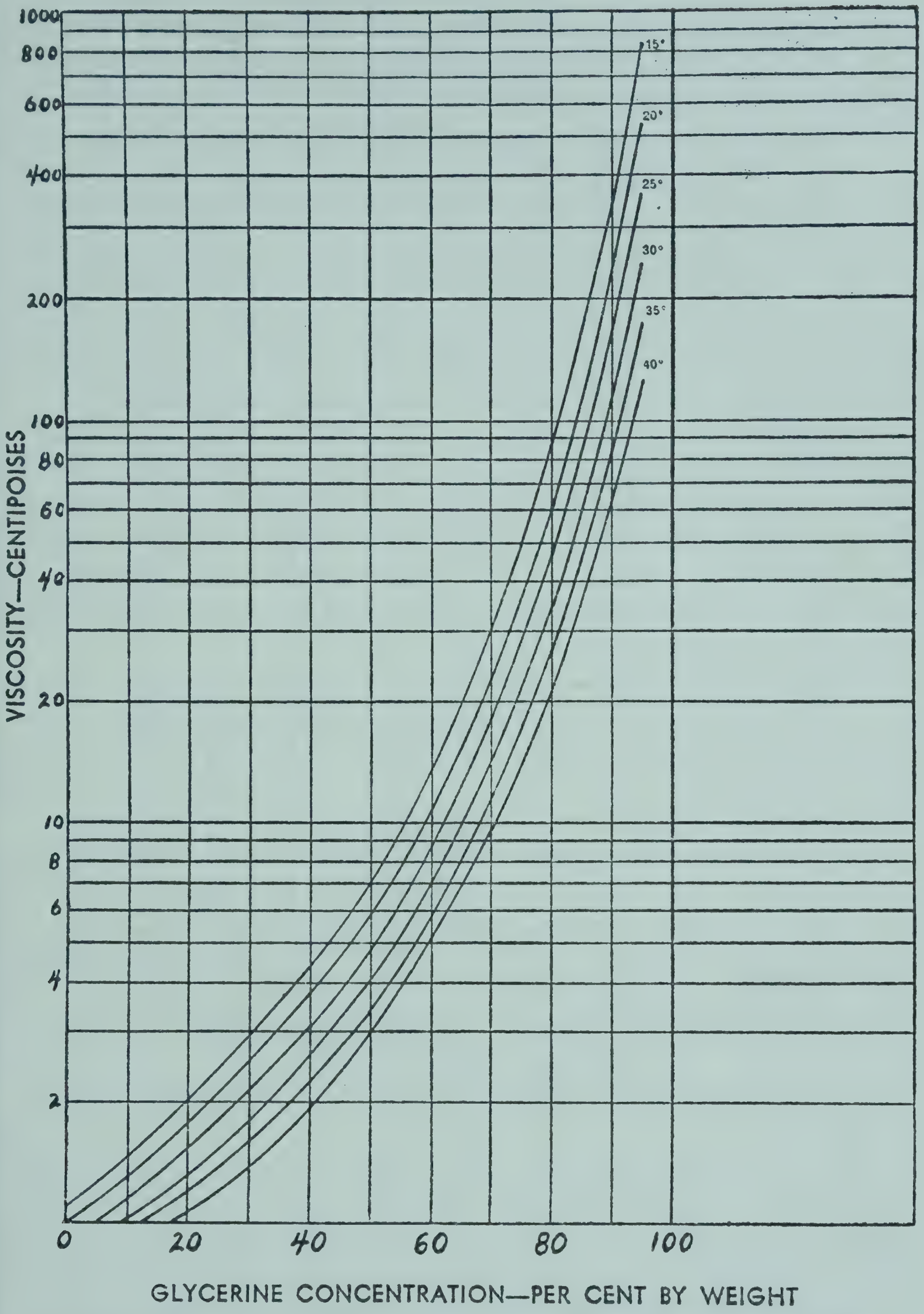


FIGURE 11.97. Glycerine Concentration vs. Viscosity at 15 to 40°C.[22]

Glycerol (1,2,3-Propanetriol, Glycerin) [$CHOH(CH_2OH)_2$]. Glycerol, an essential constituent of animal and vegetable life, was first extracted from fats by the Swedish scientist, Karl Wilhelm Scheele, in 1779 by treating olive oil with litharge. Its formula was not fully established before the work of Pelouze in 1836, and later Berthelot and Wurtz worked out its structure.

This polyhydroxy compound, among the oldest and most widely used, has up until 1948 been obtained exclusively as a by-product of the soap-making industry. To appreciate its importance, U. S. production in 1948 reached an estimated level of about 200,000,000 pounds. Pasteur, during his eminent discovery of fermentation in 1858, noted that 3.5 per cent of glycerol was present in mashes of beer and wine, and was the first to realize that it might be produced by fermentation. During World War I, Neuberg, Connstein, Ludecke and others, worked out methods of producing glycerol from the fermentation of sugar. By 1920, one or two large chemical companies launched the production of glycerol by the fermentation of molasses, but found that they could not compete in price with the glycerol made from fats and oils. This is because it is hardly possible to obtain even a 75 per cent theoretical yield even under ideal conditions. The by-products formed in this process are acetaldehyde, acetic acid, ethyl alcohol, pyruvic acid, etc. Within recent years a renewed interest in the production of glycerol by fermentation has been shown by some workers, who proposed as a potential source the use of dextrose, to be made from the hydrogenolygis[22] of corn starch.

In 1948 the first commercial production of synthetic glycerine, on a large scale, was realized by the Shell Chemical Co., utilizing petroleum derived-propylene, and chlorine as starting materials. The propylene is chlorinated to form allyl chloride, and the latter is then converted to a glycerol chlorhydrin which is hydrolyzed with an alkaline solution to glycerine.[23]

Hass and Patterson describe a method of purification for glycerol accomplished by crystallization and this method has been patented by Abel.[24] This method consists of holding 30° Beaumé glycerol at a temperature ranging from 32 to 43°F for a week. When crystallization is complete, it is removed by decantation and centrifuging. These workers had tried some 30 solvents for this purpose and found that *n*-butanol produced the best results. The shortcomings of this method lie in the difficulty to obtain seed crystals.

Glycerol is a clear, colorless, syrupy liquid with a faint odor and sweetish taste. It is highly hygroscopic, being able to absorb about 50 per cent of its weight of water. It is miscible in all proportions with water, alcohols, ketones, and glycols, and although insoluble in most organic solvents, it will dissolve some inorganic salts, oils, fats, tars and aniline dyes. This trihydric alcohol has weak acidic properties, which enable it to form salts. Since it is both a primary and secondary alcohol, it reacts to form ethers and esters.

Among its many and varied uses, one of the most important is in the manufacture of explosives. It is used as an antiseptic, as a moistening and sweetening agent for tobacco, and as an antifreeze. Its emollient, hygroscopic, penetrating, and softening properties are utilized in the textile

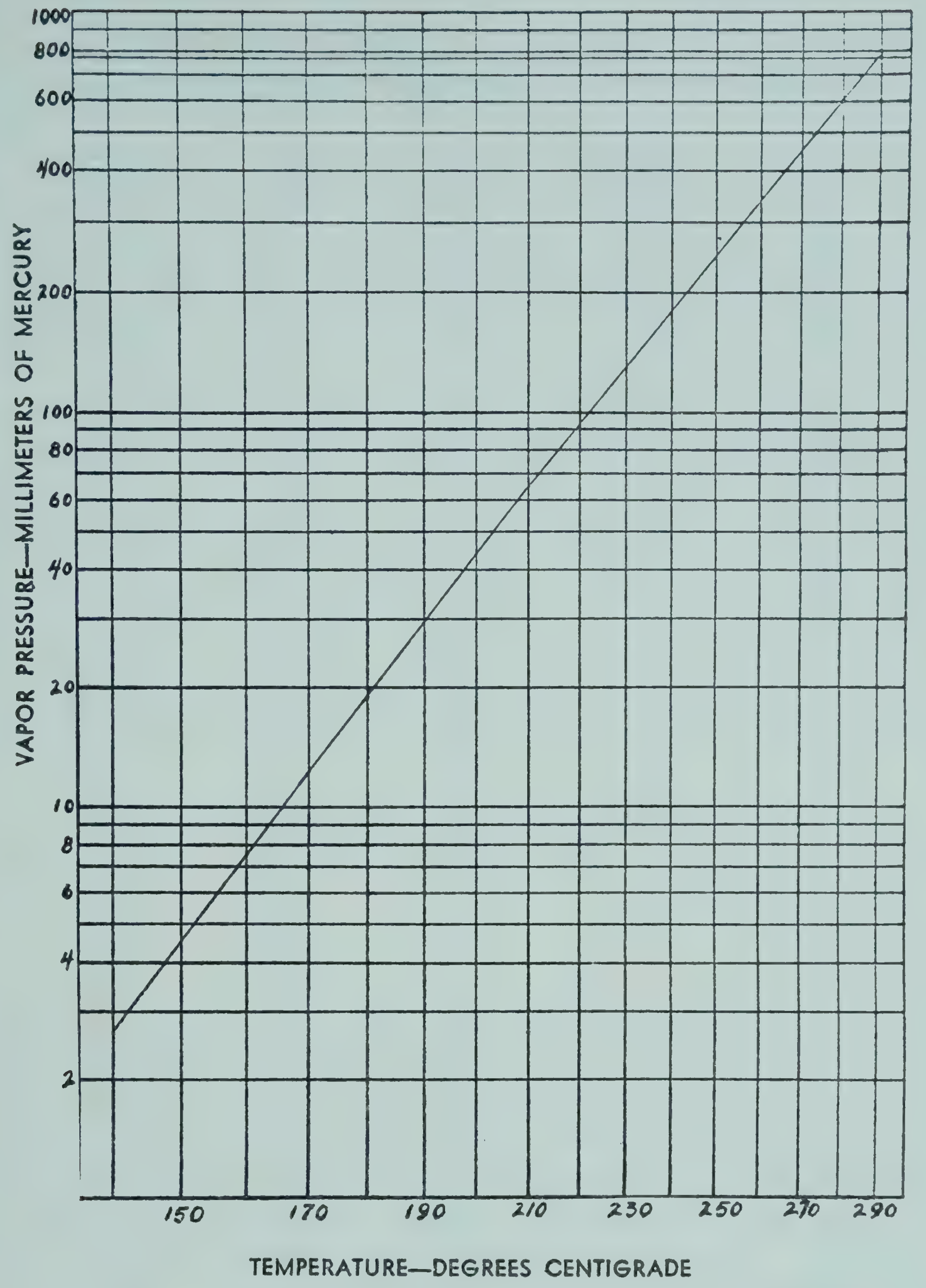


FIGURE 11.98. Vapor Pressure of Glycerine vs. Temperature.[22]

paper and leather industries, as well as in such preparations as cosmetic, toilet, and medicinal compounds, in dyes, colors, ink pastes, glues, soaps, carbon paper, and polishes, etc. It is a plasticizer for cellophane, a sizing agent for rayon, an ingredient in mercerizing liquors, and a vehicle for food color concentrates. It is used in soft drinks and hard liquors because it adds "smoothness" to the drink, and as a constituent of synthetic resins.

Boiling point	290°C
Freezing point	17.9°C
Specific gravity at 20/20°C	1.2633
Color	Water-white

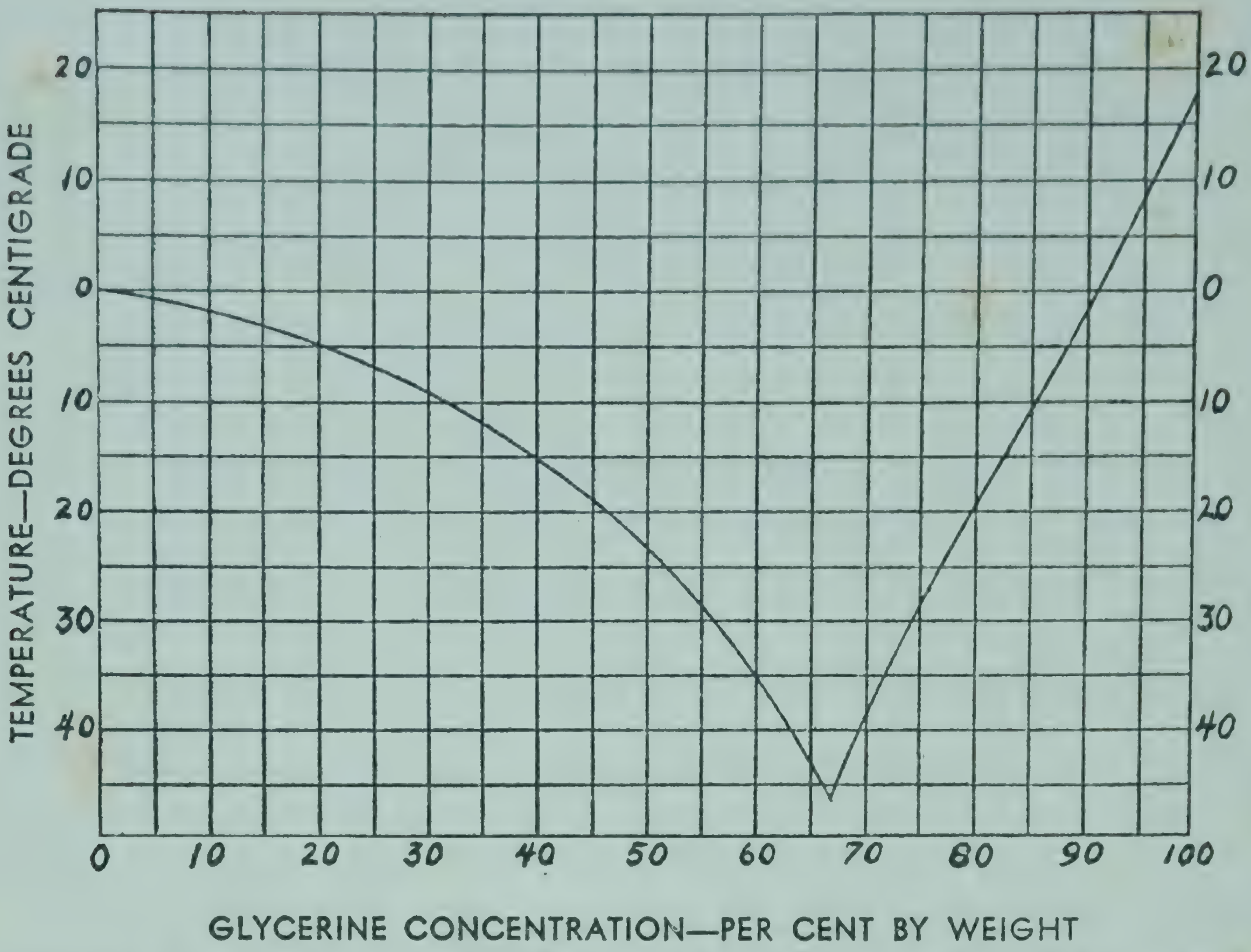


Figure 11.99. Freezing Point Diagram for Glycerine-Water Solutions.[22]

Terpene Alcohols

A mixture of substances known as pine oils is grouped under the classification of terpene alcohols. The Hercules Powder Company manufactures a number of pine oils which are designed especially as solvents for the paint and varnish industry. Generally these pine oils are added to petroleum thinners for the purpose of increasing their solvent action and imparting a pleasant odor. They are used as wetting agents in the grinding of pigments and their presence in varnishes and enamels improve flow and levelling properties.

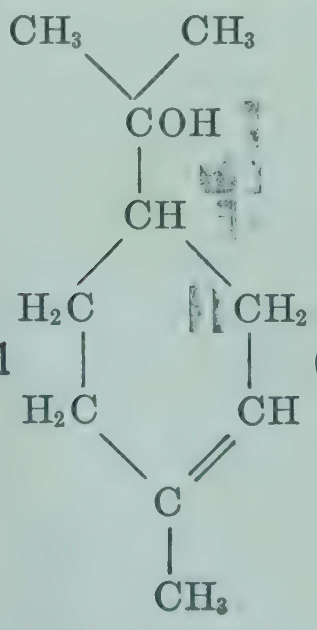
Alpha-terpineol  (terpene) is a tertiary alcohol boiling at

TABLE 11.22.—TABLES FOR SPECIFIC GRAVITY AND PER CENT GLYCEROL[26]

Glycerol	Apparent Specific Gravity			True Specific Gravity		
Per Cent	15.5/15.5° C.	20/20° C.	25/25° C.	15.5/15.5° C.	20/20° C.	25/25° C.
100	1.2653	1.2636	1.2620	1.2650	1.2633	1.2617
99	1.2627	1.2610	1.2594	1.2624	1.2607	1.2591
98	1.2602	1.2584	1.2568	1.2598	1.2581	1.2565
97	1.2576	1.2558	1.2542	1.2573	1.2555	1.2539
96	1.2550	1.2533	1.2516	1.2547	1.2530	1.2514
95	1.2524	1.2507	1.2491	1.2521	1.2504	1.2488
94	1.2498	1.2481	1.2464	1.2495	1.2478	1.2461
93	1.2471	1.2454	1.2438	1.2468	1.2451	1.2435
92	1.2445	1.2428	1.2411	1.2442	1.2425	1.2408
91	1.2418	1.2402	1.2385	1.2415	1.2398	1.2382
90	1.2392	1.2375	1.2358	1.2389	1.2372	1.2356
89	1.2365	1.2349	1.2332	1.2362	1.2346	1.2329
88	1.2339	1.2322	1.2305	1.2336	1.2319	1.2302
87	1.2312	1.2295	1.2279	1.2309	1.2293	1.2276
86	1.2285	1.2269	1.2252	1.2283	1.2266	1.2249
85	1.2259	1.2242	1.2225	1.2256	1.2239	1.2223
84	1.2232	1.2215	1.2199	1.2230	1.2213	1.2196
83	1.2205	1.2189	1.2172	1.2203	1.2186	1.2169
82	1.2179	1.2162	1.2145	1.2176	1.2159	1.2143
81	1.2152	1.2135	1.2119	1.2150	1.2133	1.2116
80	1.2126	1.2109	1.2092	1.2123	1.2106	1.2090
79	1.2098	1.2081	1.2065			
78	1.2071	1.2054	1.2038			
77	1.2044	1.2027	1.2011			
76	1.2016	1.1999	1.1984			
75	1.1989	1.1972	1.1956	1.1986	1.1970	1.1954
74	1.1961	1.1945	1.1929			
73	1.1934	1.1917	1.1902			
72	1.1907	1.1890	1.1875			
71	1.1879	1.1863	1.1848			
70	1.1852	1.1835	1.1821	1.1849	1.1833	1.1818
69	1.1824	1.1808	1.1793			
68	1.1796	1.1780	1.1766			
67	1.1768	1.1753	1.1738			
66	1.1741	1.1725	1.1711			
65	1.1713	1.1698	1.1683	1.1711	1.1696	1.1681
64	1.1685	1.1670	1.1656			
63	1.1657	1.1643	1.1628			
62	1.1630	1.1615	1.1601			
61	1.1602	1.1587	1.1573			
60	1.1574	1.1560	1.1546	1.1572	1.1558	1.1544
59	1.1546	1.1532	1.1518			
58	1.1519	1.1505	1.1491			
57	1.1491	1.1477	1.1464			
56	1.1463	1.1450	1.1436			
55	1.1435	1.1422	1.1409	1.1434	1.1420	1.1407
54	1.1408	1.1394	1.1381			
53	1.1380	1.1367	1.1354			
52	1.1352	1.1339	1.1326			
51	1.1324	1.1312	1.1299			
50	1.1297	1.1284	1.1272	1.1295	1.1283	1.1270
49	1.1269	1.1257	1.1245			
48	1.1242	1.1230	1.1218			
47	1.1215	1.1203	1.1191			
46	1.1188	1.1176	1.1165			
45	1.1160	1.1149	1.1138	1.1159	1.1147	1.1136
44	1.1133	1.1122	1.1111			
43	1.1106	1.1095	1.1084			
42	1.1079	1.1068	1.1057			
41	1.1051	1.1041	1.1031			
40	1.1024	1.1013	1.1004	1.1023	1.1012	1.1003
39	1.0997	1.0987	1.0977			
38	1.0970	1.0960	1.0951			
37	1.0943	1.0933	1.0924			
36	1.0916	1.0907	1.0898			
35	1.0889	1.0880	1.0871	1.0888	1.0879	1.0870
34	1.0862	1.0853	1.0845			
33	1.0835	1.0827	1.0819			

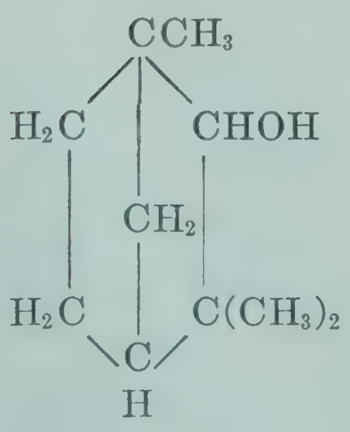
TABLE 11.22—TABLES FOR SPECIFIC GRAVITY AND PER CENT GLYCEROL—(*Continued*)

Glycerol *Per Cent*	Apparent Specific Gravity 15.5/15.5° C.	20/20° C.	25/25° C.	True Specific Gravity 15.5/15.5° C.	20/20° C.	25/25° C
32	1.0808	1.0800	1.0792			
31	1.0781	1.0773	1.0766			
30	1.0754	1.0747	1.0739	1.0753	1.0746	1.0738
29	1.0728	1.0721	1.0713			
28	1.0702	1.0695	1.0688			
27	1.0676	1.0669	1.0662			
26	1.0650	1.0643	1.0637			
25	1.0624	1.0617	1.0611	1.0623	1.0616	1.0611
24	1.0598	1.0591	1.0586			
23	1.0571	1.0565	1.0560			
22	1.0545	1.0540	1.0535			
21	1.0519	1.0514	1.0509			
20	1.0493	1.0488	1.0484	1.0492	1.0487	1.0483
19	1.0468	1.0463	1.0459			
18	1.0443	1.0438	1.0434			
17	1.0418	1.0413	1.0410			
16	1.0392	1.0388	1.0385			
15	1.0367	1.0363	1.0360	1.0367	1.0363	1.0360
14	1.0342	1.0339	1.0336			
13	1.0317	1.0314	1.0311			
12	1.0292	1.0289	1.0286			
11	1.0266	1.0264	1.0262			
10	1.0241	1.0239	1.0237	1.0241	1.0239	1.0237
9	1.0217	1.0215	1.0213			
8	1.0193	1.0191	1.0190			
7	1.0169	1.0167	1.0166			
6	1.0145	1.0143	1.0142			
5	1.0120	1.0119	1.0118	1.0120	1.0119	1.0118
4	1.0096	1.0095	1.0095			
3	1.0072	1.0072	1.0071			
2	1.0048	1.0048	1.0047			
1	1.0024	1.0024	1.0023			

210°C. The commercial grade is made from turpentine and terpene hydrate. It is a powerful solvent for fossil resins, kauri, pontianac, manila, synthetic resins, waxes, oils and so forth. It will dissolve many of these resins without "pre-melting" of the resin. In fact, it is used in the terpineol process for the solution of resins and gums without loss of weight. It is used as a mutual solvent for resins and cellulose esters and ethers.

Specific rotation	+7 to +11°
Freezing point	27 to 32°C
Specific gravity	0.939–0.942
Boiling range	210 to 221°C

Fenchyl alcohol



is a solvent for a wide variety of organic

TABLE 11.23. CRYSTALLIZATION OF GLYCEROL FROM VARIOUS SOLVENTS[27]

SOLVENT TESTED	RESULT	RATE OF CRYSTALIZATION
Methanol	[a]	Slow
Ethanol	[a]	Slow
1-Propanol	[a]	Slow but complete
2-Propanol	[a]	Slow
1-Butanol	[a]	Fairly rapid and complete
1-Pentanol	[a]	Fairly rapid
2,3-Butylene glycol	Sol.	Slow
Diethylene glycol	Sol.	Slow
Triethylene glycol	Sol.	Slow
2-Methoxyethanol	[a]	Very slow
2-Ethoxyethanol	Sol.	Very slow
2-Butoxyethanol	[a]	Slow
2-(2-Ethoxy)-ethoxyethanol	Sol.	Very slow
2-(2-Butoxy)-ethoxyethanol	[a]	None
Furfuryl alcohol	[a]	Very slow
2,2′-Dihydroxydiethyl ether	Sol.	Very slow
Aminoethanol	Sol.	Slow but complete
Triethanolamine	Sol.	
Diethylamine	Sol.	Fairly rapid
Liquid ammonia	Sol.	Very rapid and complete
Trimethylene glycol	[a]	Slow
Propylene glycol	[a]	Slow
Diacetone	Partially sol.	None
Furfural	Insol.	
2,2′-Dichlorodiethyl ether	Insol.	
Terpineol	Insol.	
Ethyl acetoacetate	Insol.	
Ethyl acetate	Insol.	
Chloroform	Insol.	
Carbon disulfide	Insol.	

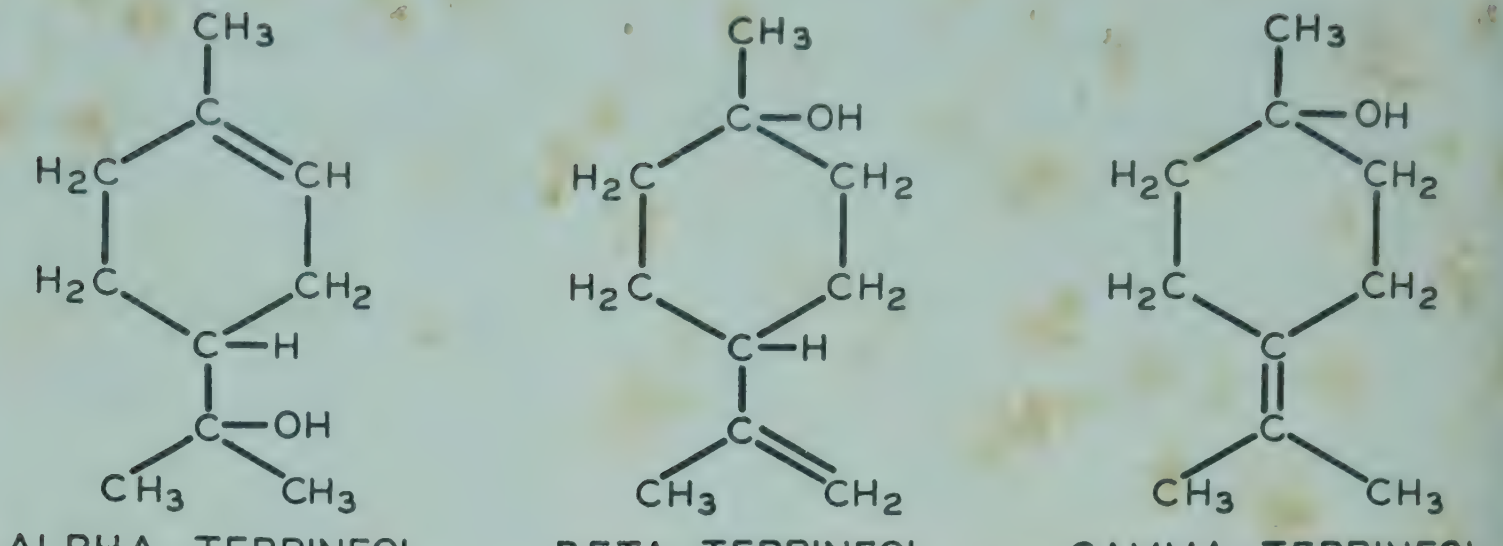
[a] Solubility not tested.

materials. It is used in organic synthesis.

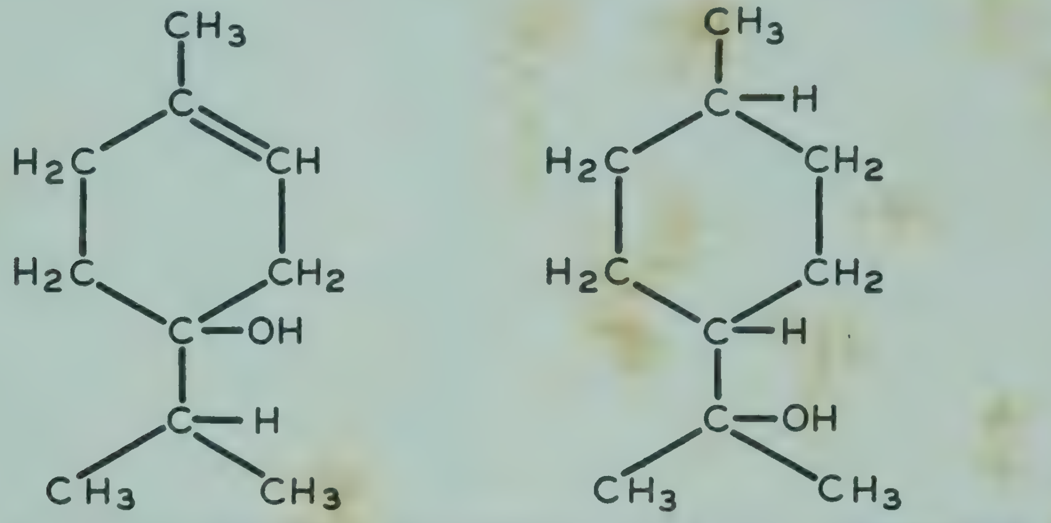
Specific rotation	−0.1°
Freezing point	30–34°C
Specific gravity	0.962 (approx.)
Boiling range	198–204°C

Hydroabietyl Alcohol

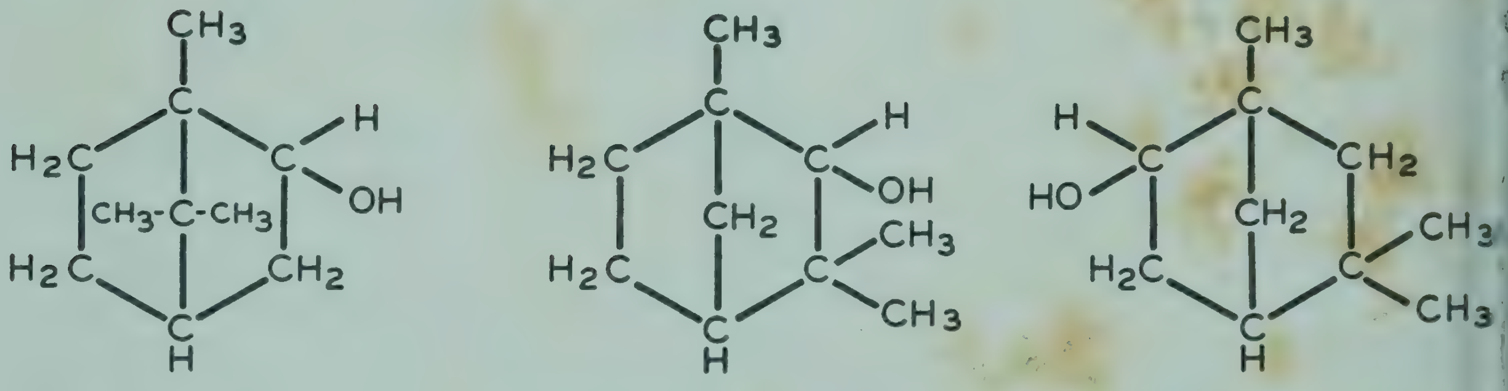
This primary monohydric alcohol is a mixture of related alcohols composed mainly of dihydroabietyl alcohol. It also includes dehydroabietyl, tetrahydroabietyl and abietyl alcohols which differ only in their degree of saturation in the molecular structure. Made from rosin, it may be called



ALPHA-TERPINEOL BETA-TERPINEOL GAMMA-TERPINEOL



4-TERPINENOL DIHYDRO-ALPHA-TERPINEOL



BORNEOL FENCHYL ALCOHOL ISOFENCHYL ALCOHOL

FIGURE 11.100. Structural Formulae of Terpene Alcohols.[28]

a "resin alcohol", and it may be the starting point for the synthesis of new series of esters. It is a water-white, highly viscous, balsam-like liquid stable chemically and thermally, with no odor or taste and low volatility It becomes less viscous upon heating. It is soluble in many organic solvents such as acetone, benzene, butyl acetate, carbon tetrachloride, ethy ether, ethyl alcohol, butyl alcohol, glacial acetic acid, methyl acetate methyl alcohol, petroleum ether, turpentine, "Varsol," and xylene, bu insoluble in water. It is necessary to warm it above room temperature t make this viscous substance dissolve more readily. It is also freely miscibl with ethylcellulose, polyvinyl butyral, and polyvinyl chloride, and i

(*Text continued on page 571*

TABLE 11.24. AQUEOUS GLYCERIN SOLUTIONS[22]

APPARENT SPECIFIC GRAVITY (AIR)

per cent Glycerol	25°/25°C	per cent Glycerol	25°/25°C
100	1.26201	50	1.12720
99	1.25945	49	1.12450
98	1.25685	48	1.12185
97	1.25425	47	1.11915
96	1.25165	46	1.11650
95	1.24910	45	1.11380
94	1.24645	44	1.11115
93	1.24380	43	1.10845
92	1.24115	42	1.10575
91	1.23850	41	1.10310
90	1.23585	40	1.10040
89	1.23320	39	1.09775
88	1.23055	38	1.09510
87	1.22790	37	1.09245
86	1.22520	36	1.08980
85	1.22255	35	1.08715
84	1.21990	34	1.08455
83	1.21720	33	1.08190
82	1.21455	32	1.07925
81	1.21190	31	1.07660
80	1.20925	30	1.07395
79	1.20655	29	1.07135
78	1.20380	28	1.06880
77	1.20110	27	1.06625
76	1.19840	26	1.06370
75	1.19565	25	1.06115
74	1.19295	24	1.05860
73	1.19025	23	1.05605
72	1.18755	22	1.05350
71	1.18480	21	1.05095
70	1.18210	20	1.04840
69	1.17935	19	1.04590
68	1.17660	18	1.04345
67	1.17385	17	1.04100
66	1.17110	16	1.03850
65	1.16835	15	1.03605
64	1.16560	14	1.03360
63	1.16285	13	1.03110
62	1.16010	12	1.02865
61	1.15735	11	1.02620
60	1.15460	10	1.02370
59	1.15185	9	1.02135
58	1.14915	8	1.01900
57	1.14640	7	1.01660
56	1.14365	6	1.01425
55	1.14090	5	1.01185
54	1.13815	4	1.00950
53	1.13540	3	1.00710
52	1.13265	2	1.00475
51	1.12995	1	1.00235

Bosart and Snoddy—Ind. & Eng. Chem. **19,** 506 (1927).

TABLE 11.25.—VAPOR PRESSURE*-TEMPERATURE DATA ON TERPENES AND TERPENE ALCOHOL[29]

α-Pinene		β-Pinene		Dipentene		Terpinolene		Fenchyl Alcohol		α-Terpineol	
° C.	Mm.	° C.	Mm.	° C.	Mm.	° C.	Mm.	° C.	Mm.	° C.	Mm.
21.2	4.0	24.3	3.4	21.1	1.5	40.5	1.2	59.1	2.5	83.8	5.9
22.0	4.3	24.5	3.6	21.2	1.6	45.5	4.2	63.6	3.5	89.9	8.1
22.2	4.8	24.7	3.9	55.7	11.5	58.2	6.5	64.4	3.9	90.6	8.6
22.5	6.0	24.8	3.0	56.2	12.3	59.7	7.5	71.1	5.3	94.7	9.6
54.7	22.8	25.0	4.6	78.5	29.8	63.3	8.4	72.1	5.6	100.0	12.6
55.3	24.0	25.4	4.9	78.9	30.1	83.0	22.5	73.0	5.9	100.7	12.7
55.5	24.8	53.5	17.9	79.0	30.3	83.5	23.6	74.0	6.5	105.8	18.6
77.4	58.8	54.0	18.3	79.7	31.7	84.0	24.8	77.1	7.9	106.6	19.2
77.5	59.3	54.4	18.5	80.2	32.2	84.1	25.3	78.1	8.8	107.3	20.1
77.7	59.7	54.6	18.9	80.5	32.5	107.6	63.4	108.5	36.6	107.9	20.6
77.9	60.2	55.0	19.4	81.8	34.8	107.7	63.7	108.9	38.1	108.2	20.7
78.6	61.9	68.7	35.1	81.9	35.0	108.5	68.6	109.0	37.7	108.6	21.0
78.7	62.2	68.9	36.4	82.0	36.5	108.6	69.0	137.6	119.6	108.7	21.2
79.3	63.9	69.1	36.5	82.6	36.7	108.7	74.1	138.0	122.5	119.1	29.1
79.6	64.8	70.9	39.3	82.9	38.5	108.8	74.5	138.2	128.0	119.9	29.7
101.1	147.2	94.7	103.8	90.0	51.4	131.2	148.2	167.1	339.3	140.9	72.6
102.8	155.7	95.1	106.7	91.2	52.1	131.4	149.2	168.1	344.9	141.5	74.6
103.2	157.5	95.7	109.4	92.1	54.2	131.8	151.0	168.5	355.2	142.3	73.7
103.5	159.3	96.0	110.3	93.5	57.9	132.1	152.0	169.1	358.9	172.0	207.2
103.7	160.3	96.2	110.8	98.9	70.5	133.5	161.4	195.5	704.0	173.3	216.5
103.8	160.9	96.5	111.8	101.6	78.5	133.6	161.6	196.9	724.3	174.0	220.4
131.2	391.5	105.8	156.2	102.1	79.5	133.9	162.8	198.6	747.0	174.5	223.0
132.3	401.0	106.0	157.5	102.5	81.1	157.8	343.8	198.8	751.3	177.6	246.0
132.4	404.0	106.4	159.8	102.7	82.4	158.2	357.0	199.2	759.3	178.0	249.5
132.5	404.3	106.9	162.5	103.2	83.1	164.1	414.3			178.3	251.9
132.7	405.7	107.1	163.6	103.6	84.7	175.9	559.6			178.8	255.8
132.9	407.1	107.6	164.5	105.7	91.8	176.0	571.3			208.4	597.1
133.0	410.7	108.2	168.9	108.0	99.5	176.4	579.2			209.5	612.0
133.1	411.5	131.2	356.5	109.0	103.5	178.0	602.2			209.6	614.5
133.2	412.5	131.6	359.5	109.5	105.4	178.2	609.0			209.7	617.8
134.9	428.5	131.7	358.6	130.1	218.5	178.5	619.0			216.9	747.5
135.4	432.1	131.9	362.5	131.5	228.0	178.8	622.3			216.5	749.5
138.5	478.0	132.1	366.7	132.5	235.0	178.9	623.9				
138.8	482.0	132.6	371.9	133.3	240.0						
139.8	494.0	132.9	375.0	134.0	247.0						
140.1	501.0	133.6	379.7	134.1	250.3						
140.5	506.0	133.9	381.0	161.9	560.0						
141.2	516.0	154.7	688.5	166.4	631.5						
141.3	520.0	154.9	691.0	166.9	643.5						
141.9	528.0	155.2	693.5	167.2	648.5						
147.0	604.0	156.2	711.5	167.5	650.5						
148.0	623.0	158.0	752.0	167.9	655.5						
		158.1	757.0	168.8	667.5						
				169.1	670.5						
				169.2	683.5						
				170.3	695.5						

*Pressures for Hg. at 25° C.

Table 11.26. Physical Properties of Terpenes and Terpene Alcohols[29]

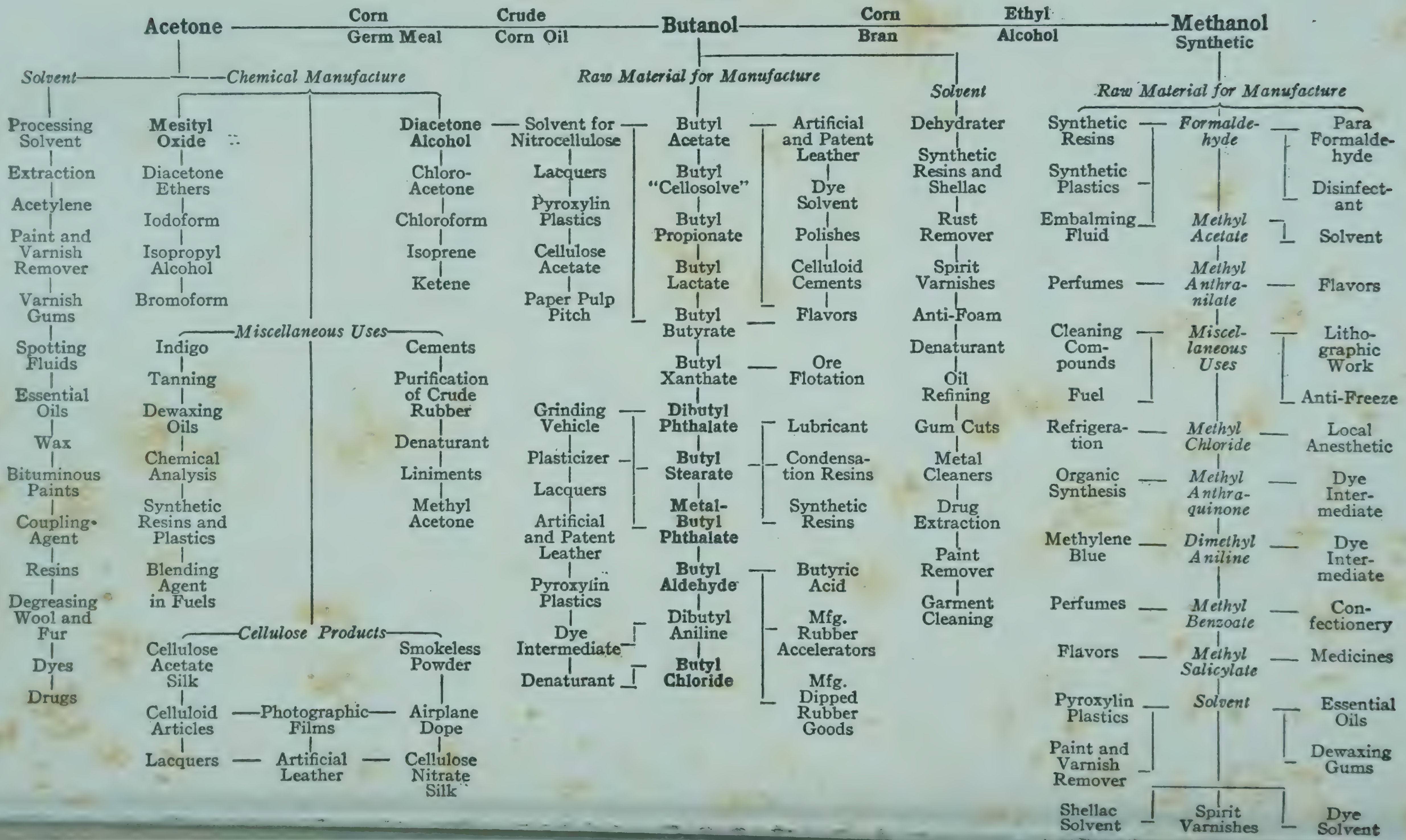
SAMPLE	BOILING RANGE		SPECIFIC GRAVITY	REFRACTIVE INDEX	OPTICAL ROTATION
	5% °C	95% °C			
α-Pinene	155	158	0.8625	1.4560	+26.50
β-Pinene[a]	160.2	163.8	0.8677	1.4709	−11.71
Dipentene	174	178	0.8481	1.4743	+ 4.2
Terpinolene	187	189.7	0.8744	1.4809	+0.2 (27.9° C)
Fenchyl alcohol	200	201.3	0.94 (35° C) 0.961 (15.6° C)[b]	1.4626	−0.1 (20° C)
α-Terpineol	218	219	(m.p. 35° C)	1.4789 (25° C)[b]	+0.19 (10% in alc.)

[a] Distilled from gum turpentine.
[b] Supercooled.

Table 11.27. Typical Analyses

	YARMOR 302 PINE OIL	YARMOR 350 PINE OIL	YARMOR 302-W PINE OIL
Specific Gravity @ 15.5/15.5°C	0.9426	0.9005	0.9214
Refractive Index @ 20°C	1.4826	1.4797	1.4792
Unpolymerized Residue	1.1%	2.4%	0.4%
Color (Lovibond 500 Amber)	3.0	2.0	3.0
Color (Lovibond 200 Red)	0.25		
Flash Point (Cleveland Open Cup)	188°F	150°F	165°F
Kauri-Butanol Solvency Value	Above 500	Approx. 500	Above 500
Aniline Point	Below −20°C	Below −20°C	Below −20°C
Viscosity (Ubbelohde @ 25°C)	18.10 cp.	2.8 cp.	6.4 cp.
Freezing Point	4°–10°C	Below 0°C	Below 0°C
Moisture	0.25%	0.20%	0.20%
A.S.T.M. Distillation Range:			
5%	213.6°C	188.5°C	198.2°C
10%	214.9°	192.0°	201.2°
30%	216.8°	195.1°	205.2°
50%	218.0°	200.0°	210.2°
70%	218.6°	207.3°	215.2°
90%	220.0°	218.0°	220.2°
95%	221.8°	220.0°	222.2°

TABLE 11.28. INDUSTRIAL USES OF ACETONE, BUTANOL, METHANOL AND THEIR DERIVATIVES[3]
(*Courtesy of Commercial Solvents Corporation*)


Acetone
Corn Germ Meal
Crude Corn Oil
Butanol
Corn Bran
Ethyl Alcohol
Methanol Synthetic
Solvent
Processing Solvent
Extraction
Acetylene
Paint and Varnish Remover
Varnish Gums
Spotting Fluids
Essential Oils
Wax
Bituminous Paints
Coupling Agent
Resins
Degreasing Wool and Fur
Dyes
Drugs
Chemical Manufacture
Mesityl Oxide
Diacetone Ethers
Iodoform
Isopropyl Alcohol
Bromoform
Diacetone Alcohol
Chloro-Acetone
Chloroform
Isoprene
Ketene
Miscellaneous Uses
Indigo
Tanning
Dewaxing Oils
Chemical Analysis
Synthetic Resins and Plastics
Blending Agent in Fuels
Cements
Purification of Crude Rubber
Denaturant
Liniments
Methyl Acetone
Cellulose Products
Cellulose Acetate Silk
Celluloid Articles
Lacquers
Photographic Films
Artificial Leather
Smokeless Powder
Airplane Dope
Cellulose Nitrate Silk
Raw Material for Manufacture
Solvent for Nitrocellulose
Lacquers
Pyroxylin Plastics
Cellulose Acetate
Paper Pulp Pitch
Grinding Vehicle
Plasticizer
Lacquers
Artificial and Patent Leather
Pyroxylin Plastics
Dye Intermediate
Denaturant
Butyl Acetate
Butyl "Cellosolve"
Butyl Propionate
Butyl Lactate
Butyl Butyrate
Butyl Xanthate
Dibutyl Phthalate
Butyl Stearate
Metal-Butyl Phthalate
Butyl Aldehyde
Dibutyl Aniline
Butyl Chloride
Artificial and Patent Leather
Dye Solvent
Polishes
Celluloid Cements
Flavors
Ore Flotation
Lubricant
Condensation Resins
Synthetic Resins
Butyric Acid
Mfg. Rubber Accelerators
Mfg. Dipped Rubber Goods
Solvent
Dehydrater
Synthetic Resins and Shellac
Rust Remover
Spirit Varnishes
Anti-Foam
Denaturant
Oil Refining
Gum Cuts
Metal Cleaners
Drug Extraction
Paint Remover
Garment Cleaning
Raw Material for Manufacture
Synthetic Resins
Synthetic Plastics
Embalming Fluid
Perfumes
Cleaning Compounds
Fuel
Refrigeration
Organic Synthesis
Methylene Blue
Perfumes
Flavors
Pyroxylin Plastics
Paint and Varnish Remover
Shellac Solvent
Formaldehyde
Methyl Acetate
Methyl Anthranilate
Miscellaneous Uses
Methyl Chloride
Methyl Anthraquinone
Dimethyl Aniline
Methyl Benzoate
Methyl Salicylate
Solvent
Spirit Varnishes
Para Formaldehyde
Disinfectant
Solvent
Flavors
Lithographic Work
Anti-Freeze
Local Anesthetic
Dye Intermediate
Dye Intermediate
Confectionery
Medicines
Essential Oils
Dewaxing Gums
Dye Solvent

miscible to a lesser degree with nitrocellulose, cellulose acetate-propionate, and cellulose acetate-butyrate. It is immiscible with polyvinyl acetate, methyl methacrylate polymers, cellulose acetate, and polystyrene. Small amounts can be usefully incorporated in chlorinated rubber.

Its primary use is in the synthesis of esters, because of its stability when heated and its resistance to oxidation. Other proposed uses are as a softening agent and plasticizer in the protective-coating industry; in adhesives, synthetic resins, and lacquers made from such materials as chlorinated rubber, ethylcellulose, vinyl polymers, and so forth; in paper coating; in varnishes; as a wetting agent; as a grinding agent for pigment pastes; in printing inks; as a wax modifier; in textile finishes; and in asphalt manufacture. Hydroabietyl alcohol must not come in contact with the skin or be used in foods. It may also be used with such water-soluble film-formers as zein, casein, soybean protein, metal caseinate, animal glue, gelatin, etc. It does not produce clear films, however, with all these substances.

Typical Properties and Specifications

Acid number	0–0.2
Bromine number	35–45
Color (50-mm tube) Lovibond	0.5 Amber
Flame point (Cleveland open cup)	217–220°C
Flash point (Cleveland open cup)	185–195°C
Hydroxyl value	5.0–5.2%
Hydroabietyl alcohol content (Based on hydroxyl value)	85–89%
Methoxyl value	0.5–1.2%
Metals (spectroscopic analysis)	nil
Saponification number (Diethylene glycol method)	5–14
Softening point	33°C
Specific gravity at 20/20°C	1.007–1.008
Refractive index at 20°C	1.528
Vapor pressure at 25°C	1.5×10^{-5} mm
100°	1.5×10^{-2} mm
200°	4.4 mm
250°	34 mm
300°	175 mm
Viscosity at 25°C	18,000–22,000 poises
35°	1,600
40°	600
50°	85

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Chapter 12

Furfural

(Furfuraldehyde, furol, furfuranecarboxylic aldehyde, pyromucic aldehyde) $[\underbrace{\mathrm{CH{:}CH{\cdot}O{\cdot}C(CHO){:}CH}}]$. Furfural was first prepared in 1830 by Dobereiner, who subjected sugar to the action of sulfuric acid and manganese dioxide. It was also made from bran, thus deriving its name (furfur, bran plus oleum, oil). Today it is principally derived from corncobs. The Quaker Oats Company was the first to produce furfural on a commercial scale.

Their method of manufacture is first to convert the pentosans to pentose sugars and then to furfural by dehydration. The pentosan-containing material is the basic source from which furfural is made and the theoretical yield is about 50 to 60 per cent, according to Peters.[1] Some have made the claim that furfural can be made from cellulosic materials, but Peters predicts that for some time to come it will continue to be made from oat, cottonseed, rice, sunflower seed hulls, corncobs, bagasse and straw. Peters also estimates that the potential annual source of raw material is about 6.5 million tons.

Furfural possesses a wide range of solvent action, dissolving most types of cellulose esters and ethers, gums, natural and synthetic resins, waxes, oils, and dyes, and many organic substances, some of which are oleic acid, carbazole and anthracene. By adding an aliphatic alcohol or ester, its solvency for cellulose derivatives will be augmented.

One of the largest uses for furfural is as a selective solvent in the purification of lubricating oils[1–5, 10, 11], in the isolation and purification of anthracene[7–9] from an admixture with phenanthrene and carbazole, and in the purification and oxidation of rosin[6, 10]. This use was first conceived by Egon Eichwald, who described it in his patent of 1925. Eight years later this method was brought into practical use. Reduced to its simplest form, the furfural refining process involves the treatment of the oil with furfural, separation of a refined oil, and an extract, followed by recovery of the solvent for reuse in the refining process. This is shown schematically in Fig. 12.1. The efficacy of the recovery process is attested by the fact that losses in refineries in which furfural is employed as a selective solvent amount to about 0.03 to 0.06 per cent of the furfural used per cycle. The

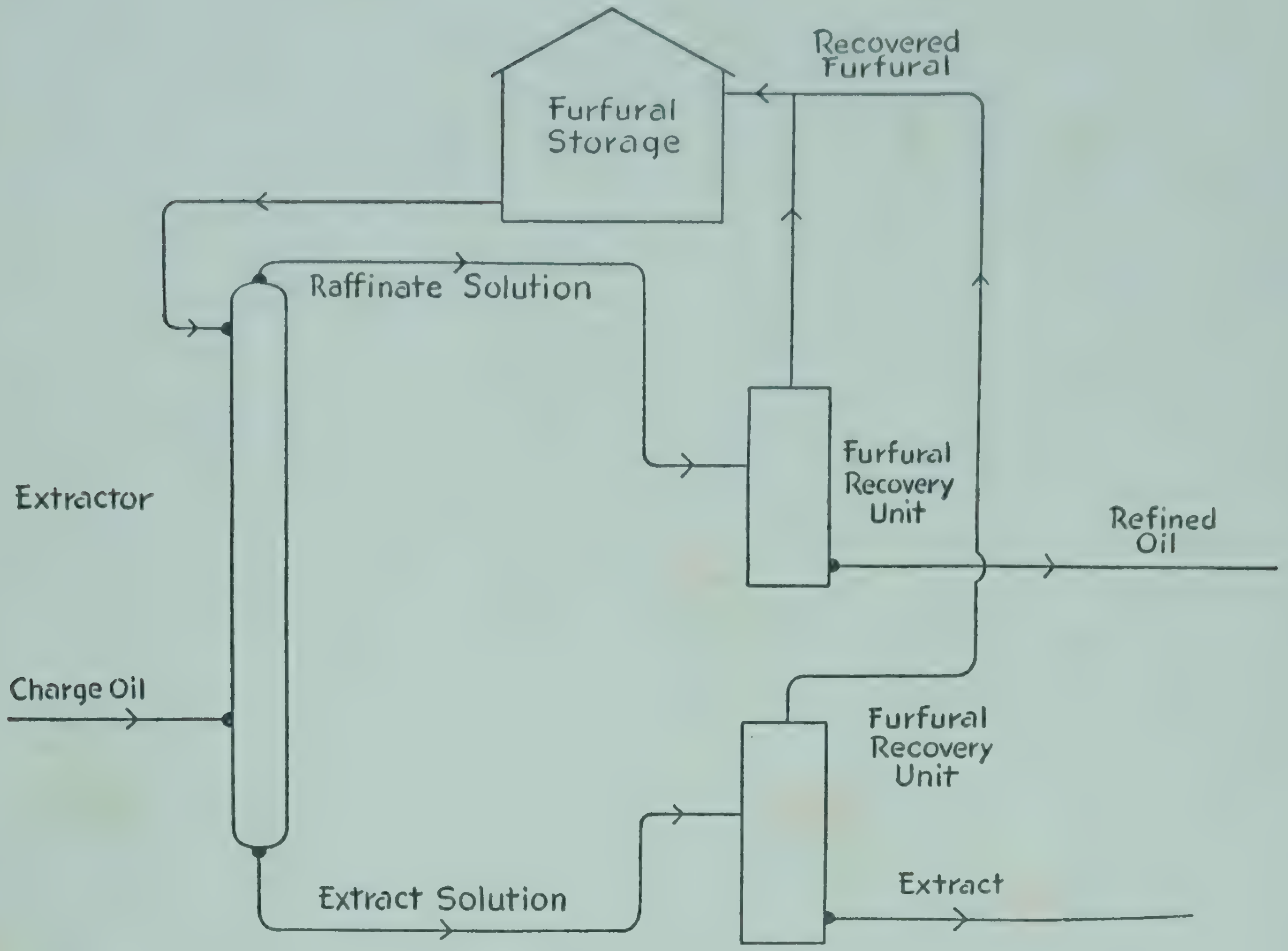
Furfural Storage
Recovered Furfural
Raffinate Solution
Extractor
Furfural Recovery Unit
Refined Oil
Charge Oil
Furfural Recovery Unit
Extract
Extract Solution

FIGURE 12.1. Furfural Solvent Refining Process.

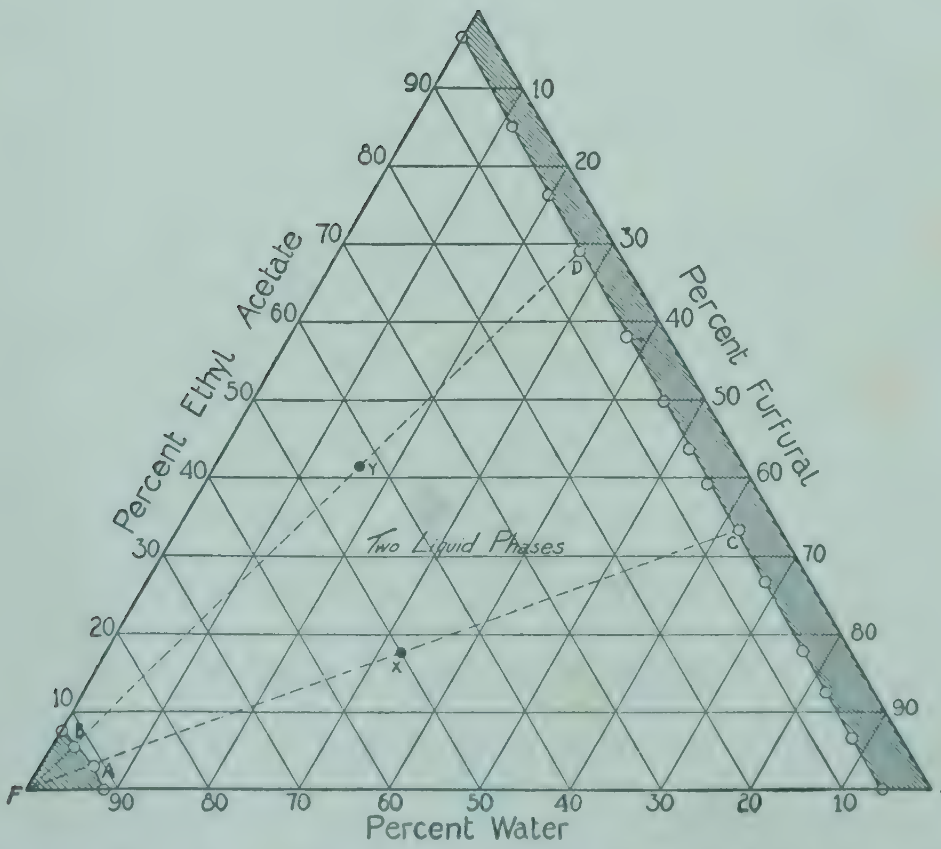

FIGURE 12.2. Miscibility Relationships of Furfural, Ethyl Acetate, and Water at 25°C.

furfural refining process gives excellent yields of oils having high viscosity indices, as well as exceptional resistance to sludging and other deterioration effected at high-temperature motor operation. The process is simple, economical, and easily controlled.

An older use for the selective solvency of furfural is for the purpose of removing colored compounds from crude wood rosin. It is also widely used in the manufacture of resinous material, where it is condensed with amines, ketones, phenols, and so forth. It is added to asphalt for its adhesive qualities with gravel and crushed stone. It is used in making vulcanization accelerators, antioxidants, dyes[14], waxes[13], and intermediates. It is a solvent for lacquers made with a cellulose ester, cellulose ether, or varnish gum base, and for such substances as formaldehyde and oleic acid. It is used as a fly-repellent, preservative, fungicide, herbicide, and tanning agent. The condensation products of furfural and ketones are sensitive to

TABLE 12.1.—SOME PHYSICAL CONSTANTS OF FURFURAL AND ITS DERIVATIVES

NAME	MELTING POINT (°C)	BOILING POINT (°C)	DENSITY d_4^{20}	REFRACTIVE INDEX
n-Amyl furoate		233	1.033	
n-Butyl furoate		227	1.0555	1.4740
n-Butyl furfuryl ether		189–190	0.955	
Ethyl furoate	34	195–7	1.1774	1.4782
Furylacrolein		200		
Furylacrylic acid		226		
Furan		31	0.937	1.4216
Furfural	−36.5	158–162	1.1598	1.4161
Furfural acetone	125	229 (decomposes)		
Furfural acetophenone		180–1 (8 mm.)		
Furfural diacetate		143–4 (20 mm.)		
Furfuraldoxime (sym.)	89			
Furfuraldoxime (anti)	73			
Furfurin	117			
Furfuryl acetate		175–7	1.1175	1.4627
Furfuryl alcohol		165–8	1.1351	1.4864
Furfuryl amine		145–6	0.955	
Furfuryl butyl ether		189–190		
Furil	162–5			
Furoin	135–9			
Furoic acid	132–3	230–2		
Furoyl chloride		170		
Hydrofuramide	115–120			
Isoamyl furoate		232	1.0335	1.4720
Methyl furoate		181	1.178	1.4869
2-Propyl furoate		211	1.075	1.4750
Tetrahydrofurfuryl acetate		84–6 (14 mm.)		
Tetrahydrofurfuryl alcohol		177–8	1.055	1.4508
Tetrahydrofurfuryl benzoate		143–5 (3 mm.)		

Table 12.2.—Solubility of Gums and Resins[12]

PRODUCT	CONGO	GUAIAC	DAMMAR	COUMARONE	ESTER GUM	SANDARAC	MASTIC	KAURI	PONTIANAC	SHELLAC
Furfural	SW	SS	SS	S	S	SS	SS	SS	SW	SS
Methyl furoate	SW	SS	SS	S	S	SW	SW	SW	SW	SS
Ethyl furoate	SW	S	SW	S	S	SW	SW	SW	SW	SS
Propyl furoate	SW	SS	SW	S	S	SW	SW	SW	SW	SS
n-Butyl furoate	SW	SS	SW	S	S	SW	SW	SS	S	SS
Isoamyl furoate	SW	SS	SW	S	S	SW	SW	SS	SS	SS
Furfuryl alcohol	SW	SS	SW	S	S	S	S	S	S	S
Furfuryl acetate	SW	SS	SW	S	S	SW	SW	SS	SW	SS
Tetrahydrofurfuryl alcohol	SS	S	SW	S	S	S	S	S	S	S

sw = swells; ss = slightly soluble; s = soluble.

Table 12.3.—Solubility of Organic Acids in Furfural[18]

ACID	WT. % SOLUBLE[a] AT:		
	0°C	25°C	40°C
Abietic (technical)	3.21	9.4	16.3
Acetic	I	I	I
Benzoic	1.2	14.8	34.3
Butyric (technical)	I	I	I
Cinnamic	0.6	4.1	10.9
Citric	0.3	3.6	9.9
Formic	I	I	I
Lactic	I	I	I
Maleic	5.1	R	R
Naphthenic acis (practical)	I	I	I
Oleic (U.S.P.)	I	I	I
Oxalic	3.2	4.8	9.1
Oxalic (anhydrous)	1.6	3.6	7.8
Palmitic (technical)	1.1	1.6	10.2
Phthalic	6.2	17.6	. .
Propionic (technical)	I	I	I
Salicylic	1.5	11.0	28.8
Sebacic (m.p., 132–133°C)	0.7	0.8	2.5
Stearic (U.S.P.)	0.3	2.1	13.1
Succinic	2.0	3.0	7.0
Tartaric	1.2	10.9	

[a] I = infinite; R = reaction.

light and are therefore utilized in photolithographic and photoengraving processes. Furfural is a wetting agent[16, 17], and its solvent and penetrating properties make it a valuable component of dyeing mixtures for wood vegetable matter, leather, shoes, textiles, and similar substances. Its penetrat-

TABLE 12.4.—SOLUBILITY OF VARIOUS SALTS IN FURFURAL[18]

FORMULA	NAME	WT. % SOL. AT 25°C
$AlCl_3$	Aluminum chloride	<0.01
$(NH_4)_2CO_3 \cdot H_2O$	Ammonium carbonate monohydrate	1.7
$(NH_4)_2MoO_4$	Ammonium molybdate	0.4
NH_4NO_3	Ammonium nitrate	0.4
$(NH_4)_2C_2O_2 \cdot 2H_2O$	Ammonium oxalate dihydrate	Insol.
$(NH_4)_2S_2O_8$	Ammonium persulfate	0.1
$NH_4H_2PO_4$	Ammonium dihydrogen *o*-phosphate	Insol.
$Ba(CH_3COO)_2 \cdot 2H_2O$	Barium acetate dihydrate	<0.01
$BaCl_2$	Barium chloride	<0.01
$Ba(OH)_2$	Barium hydroxide	<0.01
$Ba(OH)_2 \cdot 8H_2O$	Barium hydroxide octahydrate	9.0
$Ba(NO_3)_2$	Barium nitrate	0.01
BaO	Barium oxide	<0.01
BaO_2	Barium peroxide	<0.01
H_3BO_3	*o*-Boric acid	0.05
$Ca(NO_3)_2 \cdot 4H_2O$	Calcium nitrate tetrahydrate	0.44
$Ca(CH_3COO)_2$	Calcium acetate	Insol.
$Ca(CH_3COO)_2 \cdot H_2O$	Calcium acetate monohydrate	<0.01
$CaCO_3$	Calcium carbonate	0.04
$Ca_3(C_6H_5O_7)_2 \cdot 4H_2O$	Calcium citrate tetrahydrate	0.01
$CaCl_2$	Calcium chloride	0.01
$CaCl_2 \cdot 2H_2O$	Calcium chloride dihydrate	0.08
$Ca(CN)_2$	Calcium cyanide	<0.01
$Ca[C_6H_5(OH)_5CO_2]_2$	Calcium gluconate	Insol.
$Ca(OH)_2$	Calcium hydroxide	0.13
CaO	Calcium oxide	0.03
$Ca(H_2PO_4)_2 \cdot H_2O$	Monocalcium phosphate	<0.01
$CaHPO_4 \cdot 2H_2O$	Dicalcium phosphate dihydrate	<0.01
$Cr(NO_3)_3 \cdot 9H_2O$	Chromium nitrate nonahydrate	<0.01
$Co(CH_3COO)_2 \cdot 4H_2O$	Cobaltous acetate tetrahydrate	0.01
$Co(CH_3COO)_2$	Cobaltous acetate	0.02
$CoCl_2 \cdot 6H_2O$	Cobaltous chloride hexahydrate	0.5
$Cu(NO_3)_2$	Cupric nitrate	0.03
$CuSO_4 \cdot 5H_2O$	Cupric sulfate pentahydrate	Insol.
$Fe(NH_4)_3(C_6H_5O_7)_2.3H_2O$	Ferric ammonium citrate trihydrate	<0.01
$Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$	Ferrous ammonium sulfate hexahydrate	Insol.
$FeCl_3 \cdot 6H_2O$	Ferric chloride hexahydrate	20.0
$FeCl_3$	Ferric chloride	0.55
$FeC_6H_5O_7 \cdot 3H_2O$	Ferric citrate trihydrate	<0.01
$Fe(NO_3)_3 \cdot 6H_2O$	Ferric nitrate hexahydrate	0.21
$FeC_2O_4 \cdot 2H_2O$	Ferrous oxalate dihydrate	<0.01
$FeSO_4 \cdot 7H_2O$	Ferrous sulfate heptahydrate	Insol.
$Pb(CH_3COO)_2 \cdot 3H_2O$	Lead acetate trihydrate	0.05
$Pb(CH_3COO)_2$	Lead acetate	0.06
Li_2CO_3	Lithium carbonate	<0.01

TABLE 12.4—SOLUBILITY OF VARIOUS SALTS IN FURFURAL[18]—*Continued*

FORMULA	NAME	WT. % SOL. AT 25°C
$3MgCO_3 \cdot Mg(OH)_2 \cdot 3H_2O$	Magnesium basic carbonate trihydrate	0.01
$MgCl_2 \cdot 6H_2O$	Magnesium chloride hexahydrate	0.04
$Mg(NO_3)_2 \cdot 6H_2O$	Magnesium nitrate hexahydrate	0.03
MgO	Magnesium oxide	<0.01
$MgSO_4$	Magnesium sulfate	Insol.
$Mn(CH_3COO)_2 \cdot 4H_2O$	Manganese acetate tetrahydrate	0.02
$MnBO_3$	Manganese borate	0.02
MnO_2	Manganese dioxide	<0.01
$MnSO_4 \cdot 2H_2O$	Manganese sulfate dihydrate	Insol.
$HgCl_2$	Mercuric chloride	<0.01
HgO	Mercuric oxide	<0.01
NiO	Nickel monoxide	<0.01
$KBrO_3$	Potassium bromate	0.01
KBr	Potassium bromide	0.05
KCl	Potassium chloride	<0.01
KNO_3	Potassium nitrate	<0.01
K_2HPO_4	Potassium monohydrogen *o*-phosphate	0.02
$K_2S_2O_8$	Potassium persulfate	0.01
$KNaC_4H_4O_6 \cdot 4H_2O$	Potassium sodium tartrate (Rochelle salt)	<0.01
$NaCH_3COO$	Sodium acetate	<0.01
$Na(CH_3COO) \cdot 3H_2O$	Sodium acetate trihydrate	0.04
$NaHCO_3$	Sodium bicarbonate	<0.01
$NaBiO_3$	Sodium bismuthate	<0.01
$Na_2CrO_4 \cdot 4H_2O$	Sodium chromate tetrahydrate	0.05
$NaCl$	Sodium chloride	0.08
$NaCN$	Sodium cyanide	0.02
NaF	Sodium fluoride	<0.01
Na_2SiO_3	Sodium silicate	<0.01
Na_2SO_4	Sodium sulfate	Insol.
$Na_2WO_4 \cdot 2H_2O$	Sodium tungstate dihydrate	<0.01
$Sr(NO_3)_2 \cdot 4H_2O$	Strontium nitrate tetrahydrate	0.2
$ZnCl_2$	Zinc chloride	20.6
ZnO	Zinc oxide	<0.01
$ZnSO_4 \cdot 7H_2O$	Zinc sulfate heptahydrate	Insol.
$ZnSO_4$	Zinc sulfate	<0.01
ZnS	Zinc sulfide	<0.01

ing power is also utilized for resin impregnation and it is used as a paint, lacquer, and carbon remover. The solubility of a large number of acids, salts, and solvents in furfural has been worked out by Trimble[18] and is presented in the tables[18] given in this chapter.

The present commercial method of recovering furfural from a water solution is by distillation. Methods have been worked out, however, for its recovery by means of solvents. Trimble and Dunlop[19] have used a number of solvents, of which ethyl acetate has been found most comparable as an extractant to the steam-distillation method[20].

Furfural is a colorless to light amber, mobile liquid, 16 per cent heavier than water, and having an odor suggestive of oil of bitter almonds. It will turn red upon exposure. It is miscible with alcohols, ethers, ketones and most organic solvents with the exception of the paraffin hydrocarbons and glycerol and only partly soluble in water.

Typical Properties and Specifications

Acidity, as acetic	Technical 0.3%
	Refined 0.1%
Boiling point	158–162°C
Density at 60°F	1.164
100°	1.140
150°	1.110
175°	1.095
200°	1.080
250°	1.049
300°	1.019
Distillation range (Engler)	
1%, °F (min.)	300
End point, °F (max.)	335
Recovery, % (min.)	98.5
Residue, % (max.)	0.9
Loss, % (max.)	0.9
Explosive limit, lower	2.1% at 257°F
Flash Point (Cleveland Open Cup)	131–5°F
Freezing point	−34°F
Heat of Vaporization	107.51 cal./g
Purity	98.5% Technical
	99.0–99.5% Refined
Refractive index at 68°F	1.5261
Solubility in water at 20°C	8.3%
Specific gravity at 20/20°C	1.161
	1.158–1.160 Technical
	1.59–1.161 Refined
Surface tension	49 dynes/cm.
Vapor pressure at 60°F	0.035 lbs./sq. in. abs.
100°	0.130 lbs./sq. in. abs.
150°	0.540 lbs./sq. in. abs.
175°	0.950 lbs./sq. in. abs.
200°	1.650 lbs./sq. in. abs.
250°	4.40 lbs./sq. in. abs.
300°	11.50 lbs./sq. in. abs.
350°	22.50 lbs./sq. in. abs.
400°	43.5 lbs./sq. in. abs.
450°	77.0 lbs./sq. in. abs.
Viscosity at 100°F	1.35 centipoises
130°	1.09 centipoises
210°	0.68 centipoises
Weight per gallon (20°C)	9 lbs.

TABLE 12.5.—SYSTEM FURFURAL-ETHYL ACETATE-WATER AT 25°C[19]

FURFURAL %	ETHYL ACETATE %	WATER %
2.7	5.8	91.5
5.8	3.3	90.9
11.0	85.2	3.8
19.8	76.1	4.1
26.8	69.0	4.2
37.6	57.9	4.5
45.4	49.9	4.7
51.3	43.9	4.8
55.9	39.2	4.9
56.2	39.0	4.8
61.8	33.3	4.9
68.5	26.4	5.1
77.1	17.8	5.1
82.3	12.6	5.1
88.0	6.8	5.2

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Chapter 13

Ketones

Ketones have become increasingly important solvents as a result of the growth of acetate rayon and vinyl resin coatings. Although the chemical possibilities of the carbonyl group in ketones were originally discovered as long ago as 1844 by Williamson, acetone and methylethyl ketone were until recently the only ketones made on a large scale. Since 1936, however, the number of commercially available ketones has become quite large, offering advantageous solvent properties to the protective coating, plastics, and rayon industries. They are comparable to the nitrocellulose ester solvents in their range of evaporation rates and solubilities. Ketones are stable solvents having high dilution ratios for hydrocarbon diluents. They are freely miscible with most lacquer solvents and diluents and their compatibility with lacquer ingredients gives good blush resistance.

Generally, ketones are good solvents for cellulose esters and ethers and many natural and synthetic resins. The viscosity of resin solutions is found to increase in proportion to the rise of the ketone in the homologous series. The cyclic ketones are excellent resin solvents. Recently ketones have received greater attention in the manufacture of vinyl resins.[1] When used in vinyl copolymer resin solutions, the viscosity is not increased even when the solutions highly diluted with non-diluents or with greater resin concentration. A mixture of a ketone and an alcohol is a particularly useful solvent for vinyl butyral resins.

Some of the newer ketones are acetonyl acetone, cyclohexanone, diethyl ketone, diisobutyl ketone, dipropyl ketone, fenchone, methyl amyl ketone, methyl cyclohexanone, methyl hexyl ketone, methyl isobutyl ketone, mesityl oxide, ethylbutylketone, isophorone and trimethylnonanone. The availability in ample quantities of these ketones has been largely responsible for the growth in consumption of the vinyl resins. These resins are divided into four main groups: vinyl acetate polymers, vinyl butyral polymers, vinyl chloride polymers, and the vinyl chloride-vinyl acetate copolymers. The solubility of vinyl butyral resin is dependent upon the presence of residual alcohol groups in its structure.

The solution characteristics of vinyl resins have been studied extensively by Quarles,[2] who presented their behavior in numerous charts, to be found in the section on methyl isobutyl ketone. Quarles showed us that the noncyclic ketones are good solvents for the vinyl-chloride-acetate resins con-

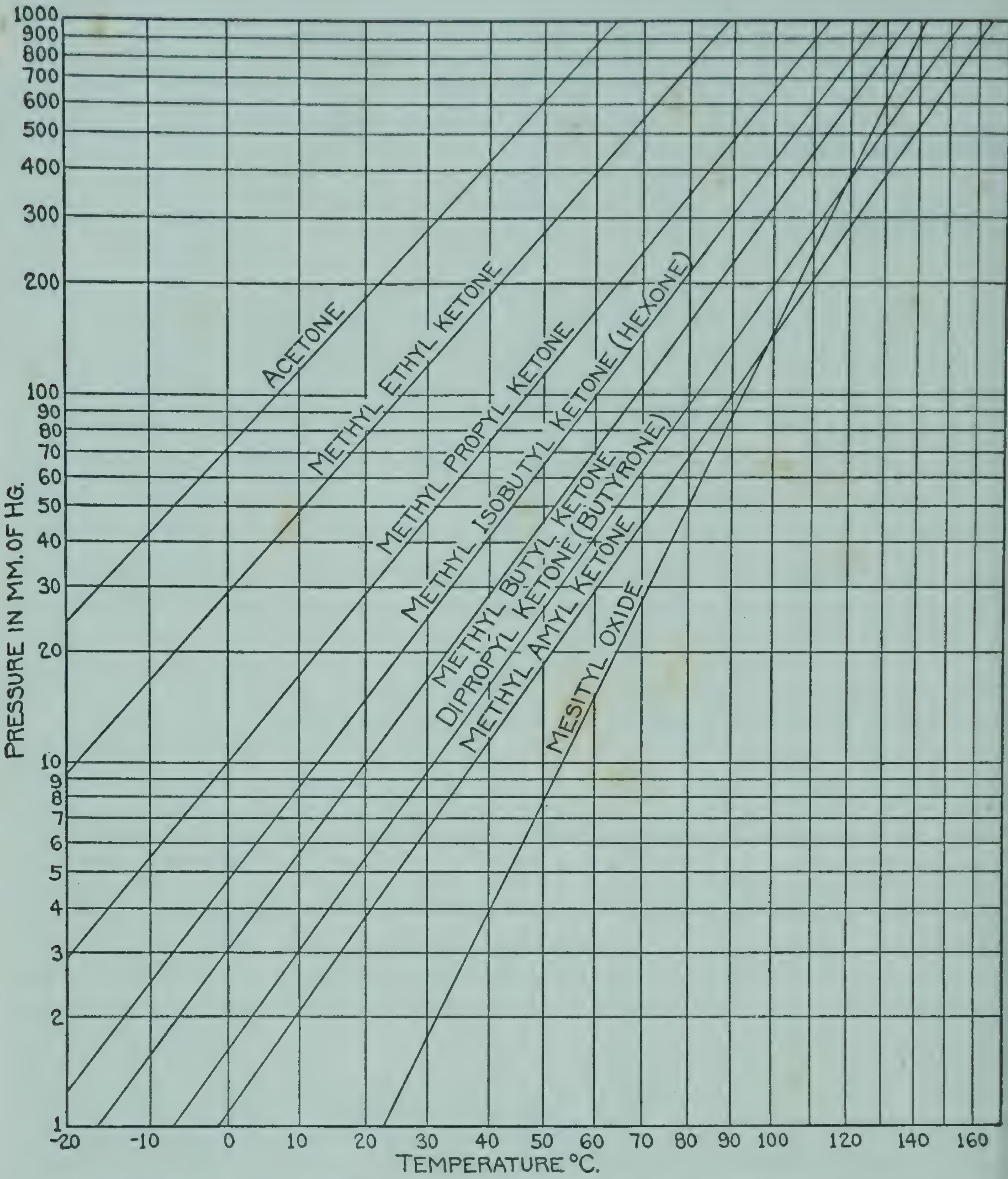


FIGURE 13.1. Vapor Pressure of Various Ketones at Different Temperatures.[5]

taining 88 per cent vinyl chloride and possessing an apparent molecular weight of 10,000. He also made a study of the solvent effect of ketones on the "Vinylite" resin VYHH. Some of the higher ketone homologs of isophorone have been suggested as plasticizers.

Acetone (Dimethyl ketone, methylacetyl, propanone-2) (CH_3—CO—CH_3). Acetone is a colorless, limpid, mobile, hygroscopic, flammable liquid having a mint-like odor. It was originally obtained by the destructive distillation of wood and the yield was later increased by converting the

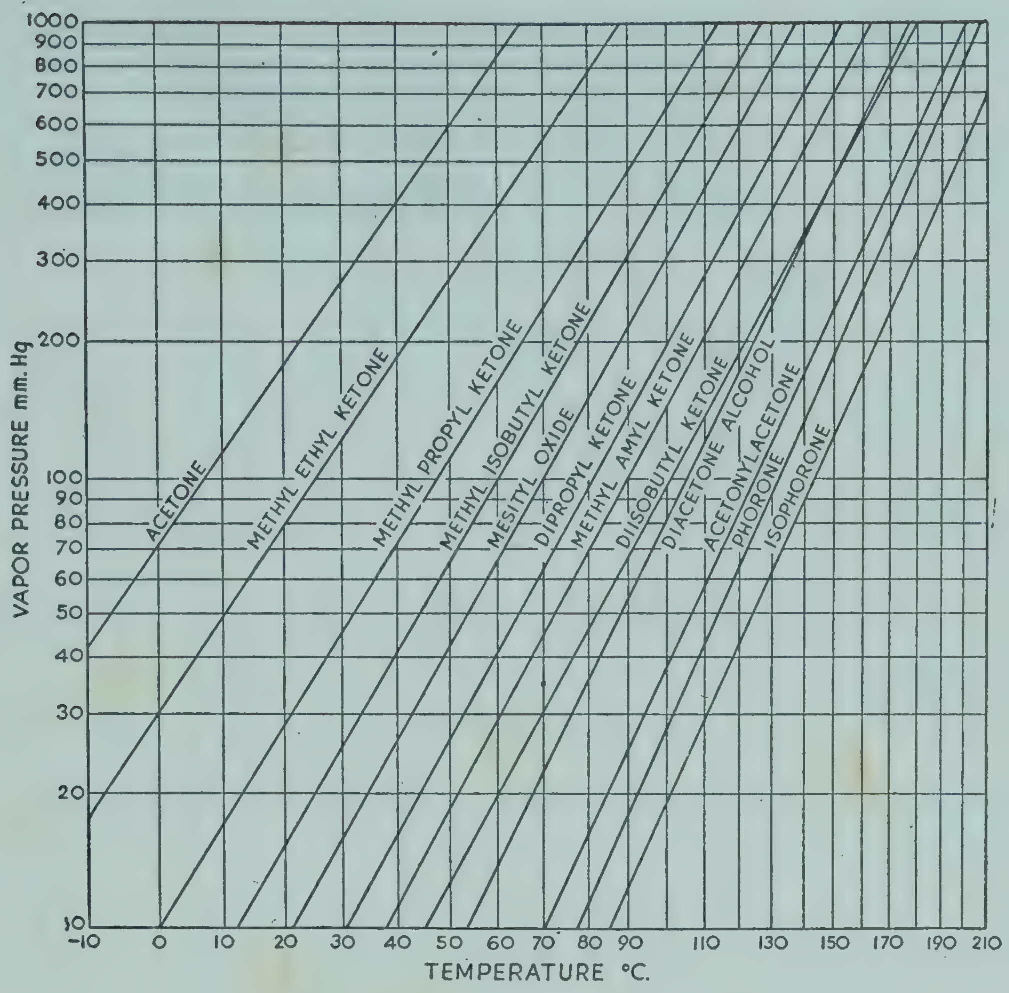


FIGURE 13.2. Vapor Pressures.

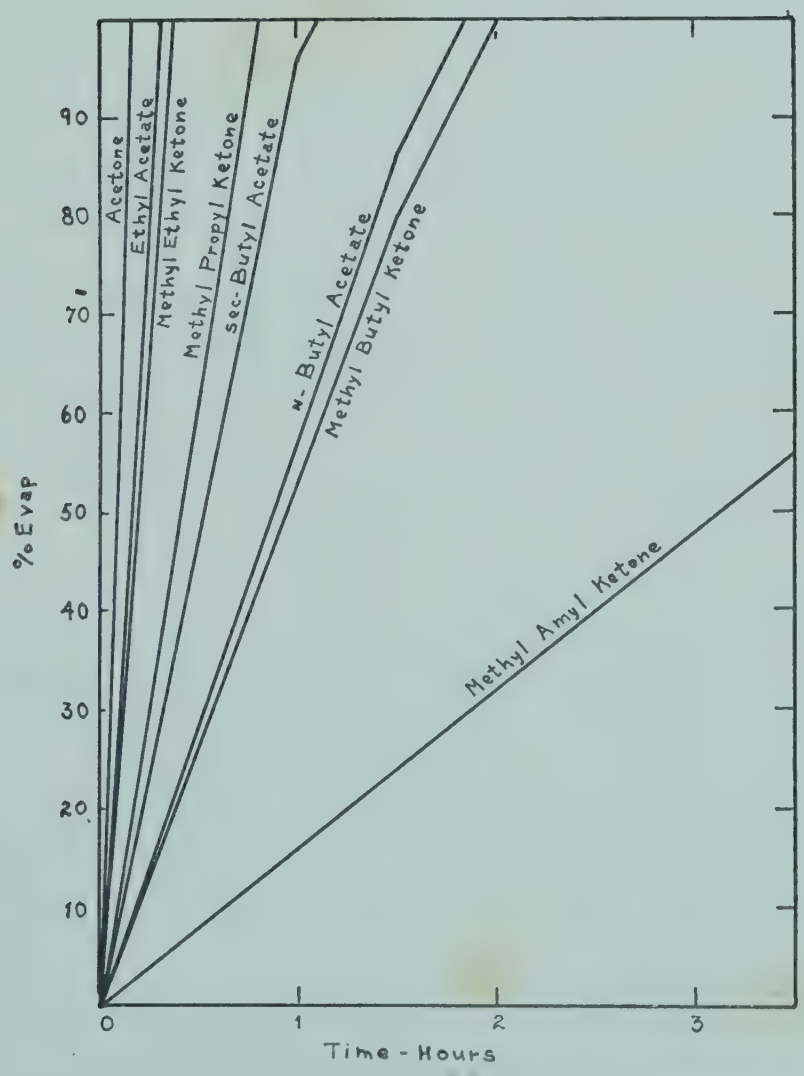


FIGURE 13.3.
Evaporation Rate of Various Ketones and Esters (Temperature 18.5–19.5°C).[4]

TABLE 13.1.—PROPERTIES OF KETONE SOLVENTS[3]

SOLVENTS	MOLECULAR WEIGHT	PURITY OF COMMERCIAL PRODUCT	SPECIFIC GRAVITY RANGE,* 20°/20°C	POUNDS PER GALLON (APPROX.), 20°C	BOILING RANGE, °C* (760 MM.)	FREEZING POINT, °C	VAPOR PRESSURE, MM. HG, 20°C
Acetone	58.08	99%	0.791–0.793	6.59	55.8–57.5	−95.0	186.2
Methyl Ethyl Ketone	72.10	99%	0.805–0.810	6.72	77–81	−86.4	71.2
Methyl *n*-Propyl Ketone	86.13		0.8064 (20°/40°C)	6.72	102	−83.5	30
Methyl *n*-Butyl Ketone	100.16		0.8298 (0°/4°C)	6.92 (0°C)	127	−56.9	10
Methyl Isobutyl Ketone	100.16	99%	0.799–0.804	6.68	111–117	−80.26	15.2
Mesityl Oxide	98.14	97%	0.853–0.856	7.12	120–135	−59	8.0
Diacetone Alcohol	116.16		0.937–0.943	7.83	130–180	−44	0.8
Methyl *n*-Amyl Ketone	114.18	95%	0.816–0.821	6.80	147–154		2.6
Diisobutyl Ketone	142.23		0.808–0.815	6.74	165–175	−46.0	1.2
Isophorone	138.20	98%	0.920–0.925	7.68	205–220	−13	0.3

acetic acid in the aqueous distillate to calcium acetate, which was further subjected to dry distillation. Acetone has also been made by the catalytic pyrolysis of acetic acid passed through heated tubes. Acetone methyl ethyl ketone and some higher ketones are now made by dehydrogenation of the corresponding olefin-derived secondary alcohols.

While synthetic acetone made from isopropanol accounts for the bulk of the output, substantial quantities of acetone are produced by the Fernbach-Strange-Weizmann fermentation process which came into extensive use about 1925 and practically eliminated the calcium acetate method of production. This fermentation process also yields *n*-butanol at the same time. Acetone can also be made by a bacterial fermentation of a giant seaweed which grows along the Pacific coast. In Canada acetone is produced synthetically from acetylene.

This widely used low-boiling ketone is one of the most powerful solvents known. It is completely miscible with water, alcohols, ethers, animal and vegetable oils, hydrocarbons, halogenated hydrocarbons, and fatty acid esters, as well as most organic solvents. It will dissolve twenty-five times its volume of acetylene at a pressure of one atmosphere, and it will continue

Table 13.1.—Properties of Ketone—*Continued*

	FLASH POINT, OPEN CUP, °F	SURFACE TENSION, DYNES/CM.	SOLUBILITY OF COMPOUND IN WATER, % BY WEIGHT	SOLUBILITY OF WATER IN COMPOUND, % BY WEIGHT	AZEOTROPE WITH WATER		RELATIVE RATE OF EVAPORATION (n-BuOAc = 1)	DILUTION RATIO			VISCOSITY OF 8% RS ½" NITROCELLULOSE SOLUTION, HERCULES CAPILLARY TUBE, 25°C (CENTIPOISES)	BLUSH RESISTANCE	
					Boiling Point, °C	Weight Per Cent of Compound		Toluene	Aromatic Petroleum Naphtha	Aliphatic Petroleum Naphtha			
Acetone	> −4	21.4	∞	∞			7.7	4.5	1.3	0.8	8	<23	1
Methyl Ethyl Ketone	34	23.5	27.0	12.5	73.4	88.7	4.6	4.4	1.4	0.9	10	45	2
Methyl n-Propyl Ketone	55		6	3.6	83.3	80.5	2.0	4.4	1.8	0.9	15	69	3
Methyl n-Butyl Ketone	95		3.5	3.7	86.4	84.3	1.0	4.0	1.7	1.1			4
Methyl Isobutyl Ketone	81	22.7	1.7	1.9	87.93	75.7	1.6	3.7	1.6	1.0	19	78	5
Mesityl Oxide	98		3.1	3.1	91.8	65.2	0.9	3.7	1.9	0.9	22	82	6
Diacetone Alcohol	151	29.8	∞	∞	99.8	12.7	0.2	3.0	1.0	0.5	153	87	7
Methyl n-Amyl Ketone	120		0.4	1.5			0.4	3.9	1.8	1.3	25	93	8
Diisobutyl Ketone	131	22.5	0.08	0.46	97.3	49.0	0.3	1.5	0.8	0.6	64	95	9
Isophorone	205		1.4	4			>0.1	6.8	1.9	1.0	104	97	10

to dissolve twenty-five times its volume of this gas for each additional atmosphere of pressure. Its solvent power varies widely for different substances as shown in the following tables.

Output of acetone has grown consistently until now its production is close to four hundred million pounds a year. First among its many uses is in the acetate rayon industry. Other important uses are as a solvent in paint and varnish removers and in the manufacture of paints, varnishes, and lacquers and acrylate resins. It is also used in the production of penicillin, in motor fuels, airplane dopes, carbon removers, as an alcohol denaturant, in degreasing wool, in artificial seasoning of wood, in lubricating compositions, in smokeless powder, in cordite, in bitumimous paint, in fabric

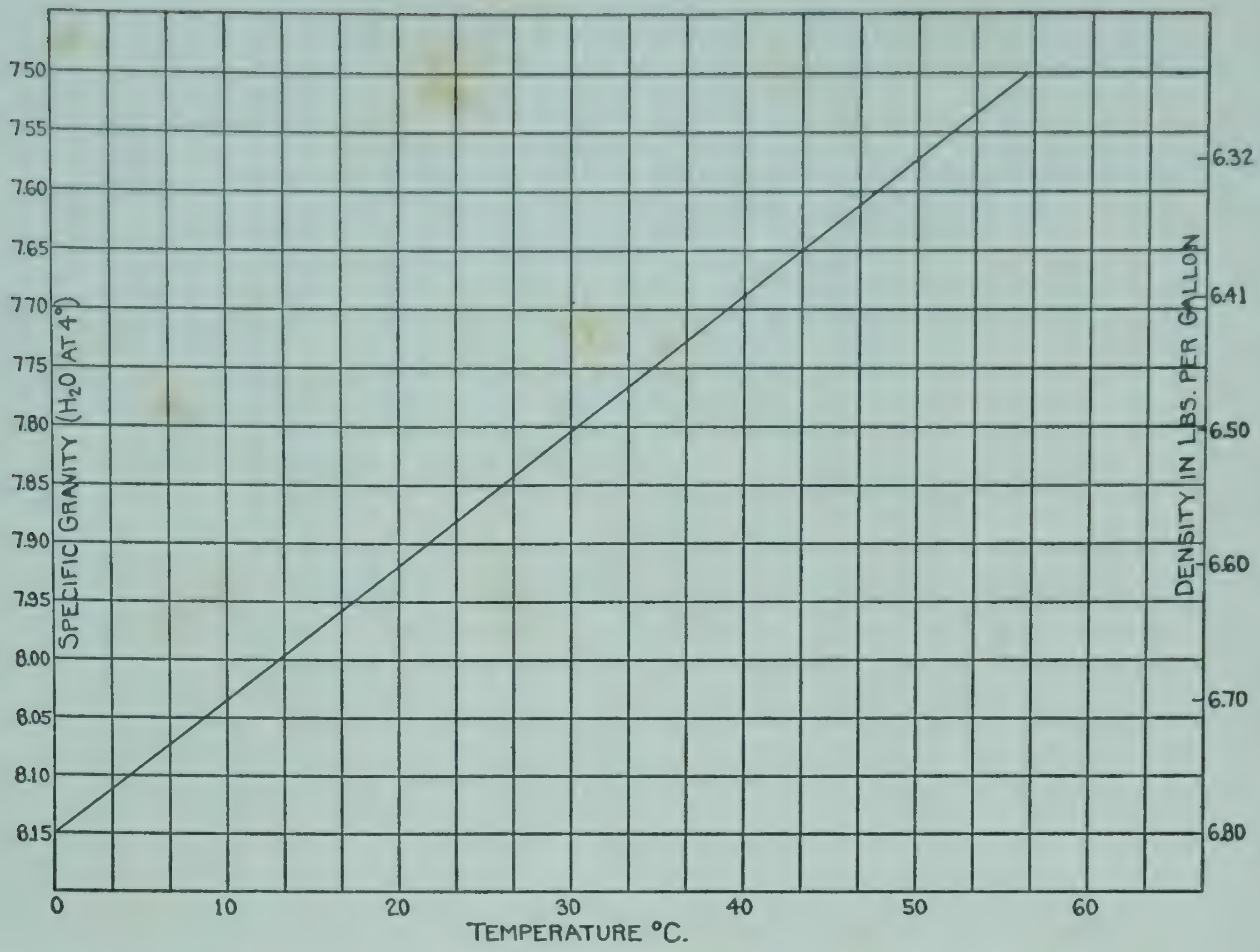


Figure 13.4. Specific Gravity and Weight per Gallon of Acetone at Various Temperatures.[5]

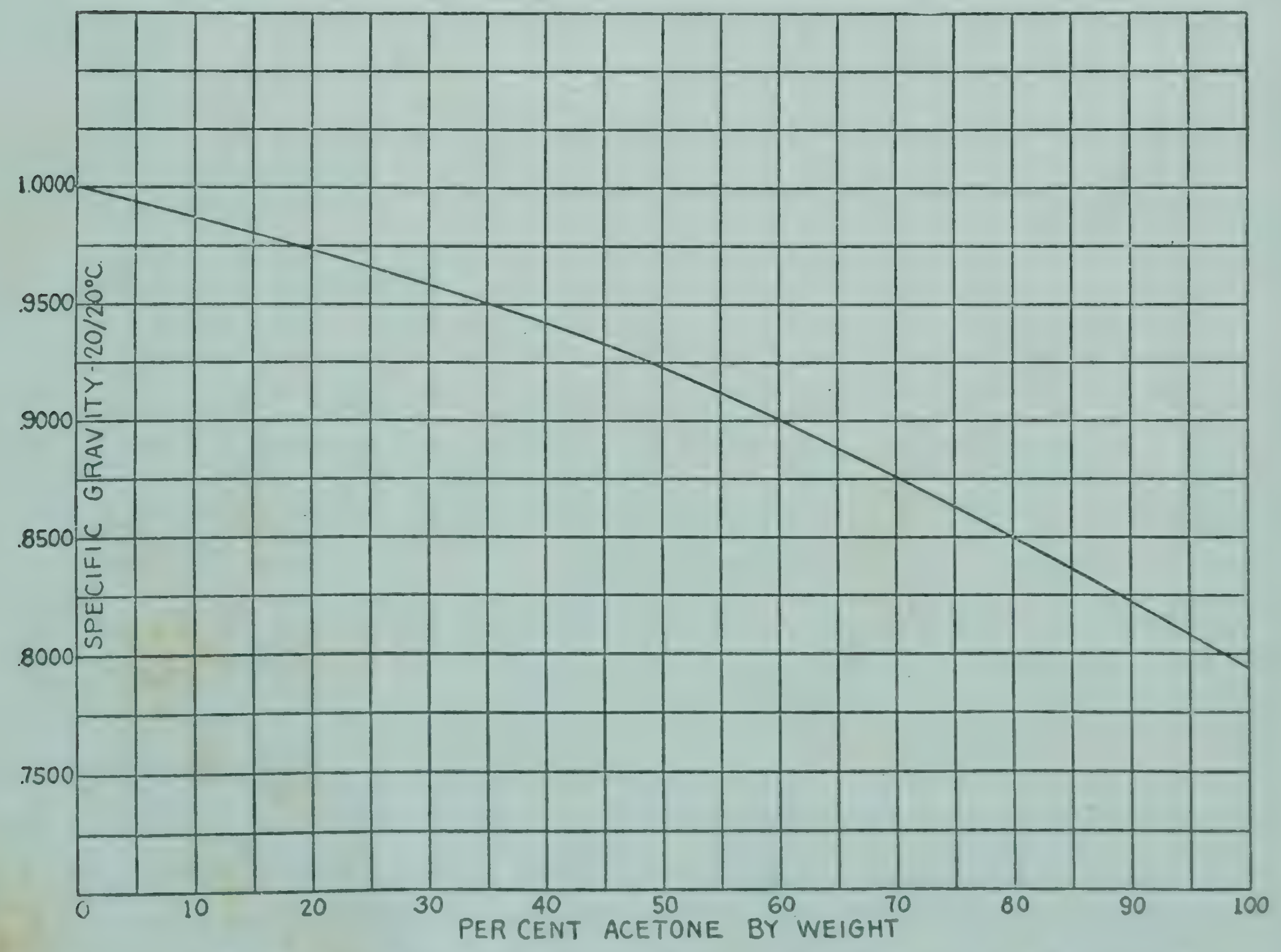


Figure 13.5. Specific Gravity of Aqueous Solutions of Acetone.[7]

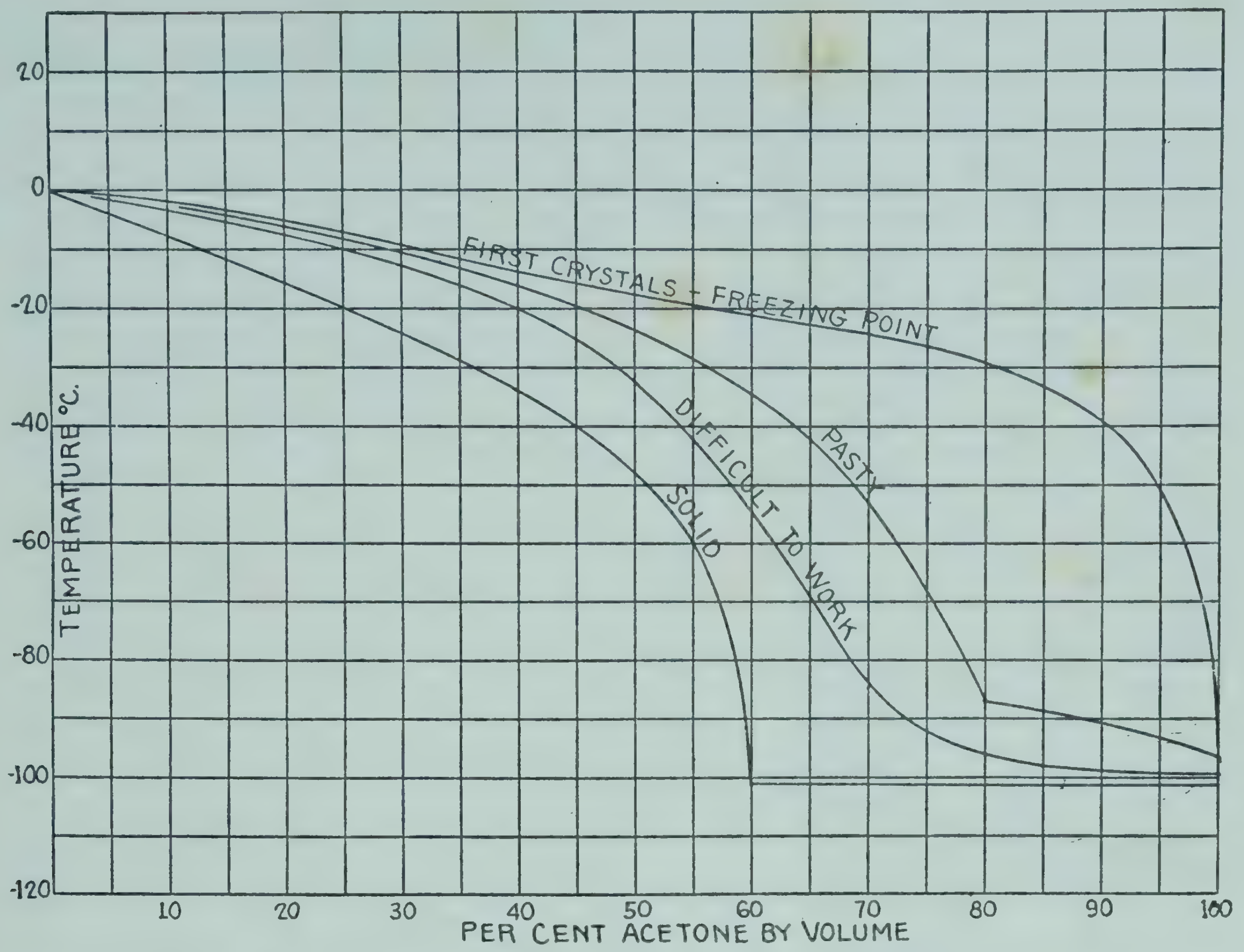


FIGURE 13.6. Low Temperature Characteristics of Aqueous Solutions of Acetone.[7]

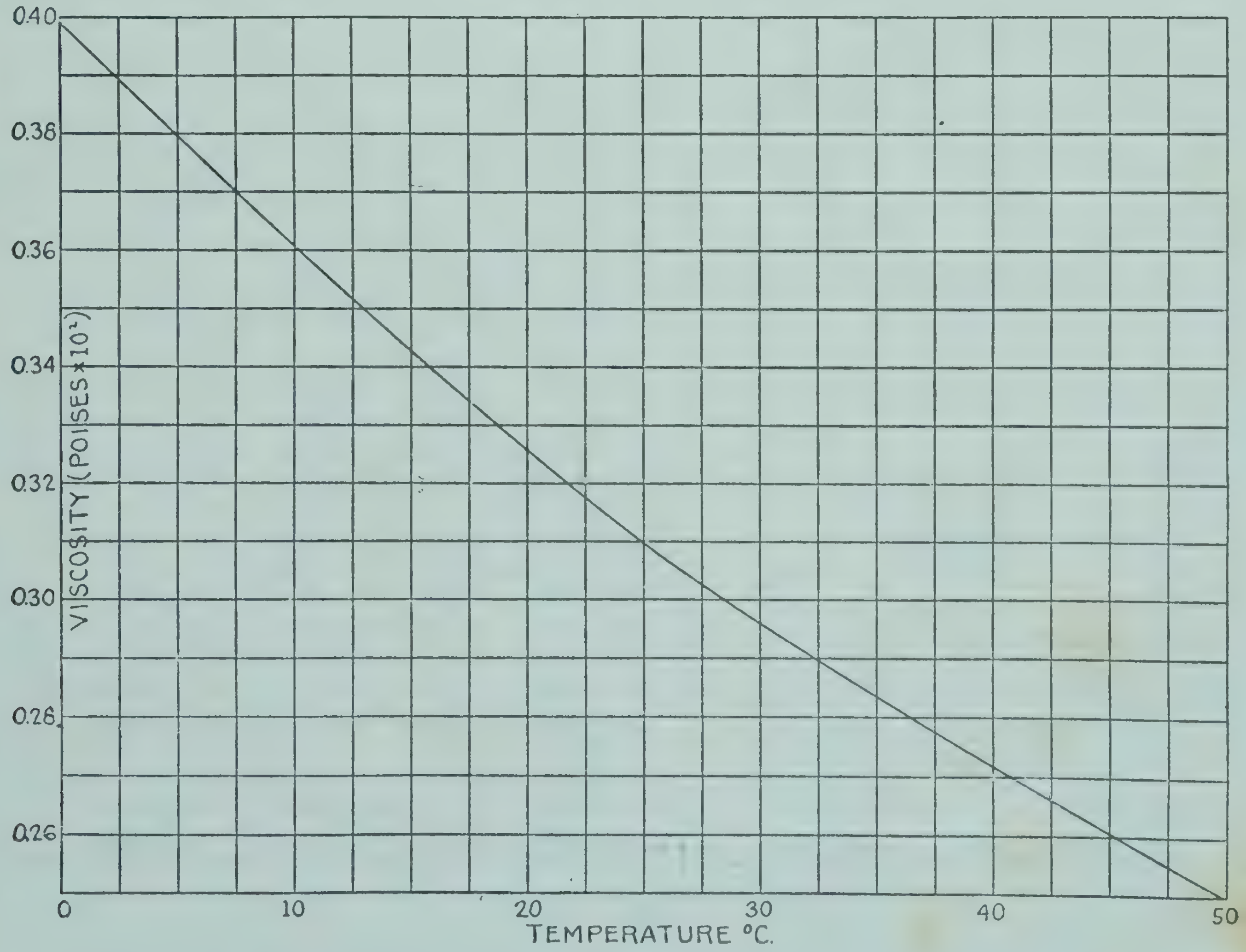


FIGURE 13.7. Viscosity of Acetone at Various Temperatures.[7]

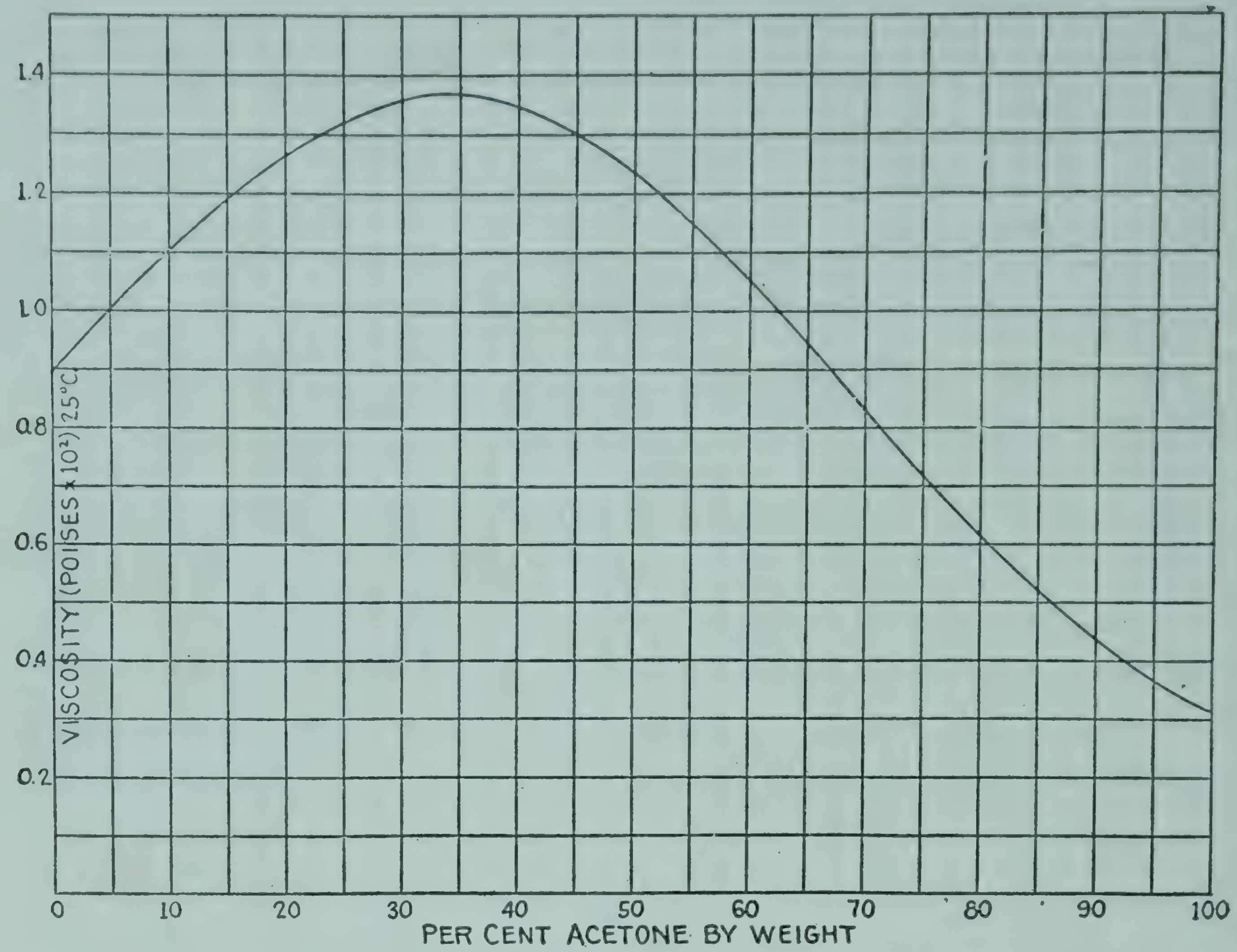


FIGURE 13.8. Viscosity of Aqueous Solutions of Acetone at 25°C.[7]

coatings, photographic film manufacture, for water-proofing compounds, and as a solvent for acetylene gas. Its uses during World War II are indicated in the table below.

(Thousands of pounds)*

USE	TOTAL		JANUARY 1–JUNE 30, 1945	JULY 1–DECEMBER 31, 1944	JANUARY 1–June 30, 1944
	Amount	Per cent			
Total Allocations	632,519	100.0	213,332	207,738	211,449
Direct Military[1]	41,790	6.6	10,434	17,720	13,636
Foreign	50,945	8.1	15,545	21,418	13,982
Other uses	539,784	85.3	187,353	168,600	183,831
Chemical manufacture	263,270	41.6	90,218	79,356	93,696
Solvents	[2]89,933	14.2	32,095	28,389	29,449
Coated fabrics and rayons	70,996	11.2	23,781	23,921	23,294
Drugs and pharmaceuticals	37,565	6.0	12,658	12,023	12,884
Resins and plastics	31,095	4.9	11,030	10,220	9,845
Rubber manufacture	16,566	2.6	5,178	5,481	5,907
Photography	8,908	1.4	3,212	2,731	2,965
Miscellaneous uses and small orders	21,451	3.4	9,181	6,479	5,791

[1] End-use data not available.

[2] Of this amount, 22,365,000 pounds was used as a solvent for acetylene.

* "Facts for Industry," U. S. Bureau of the Census.

Typical Properties and Specifications

Boiling point at 760 mm	56.1°C
Coefficient of expansion	0.00080 per °F
Color	Water-white
Critical density	0.238
Critical pressure	47 atm.
Critical temperature	235°C
Dielectric constant at 17°C	20.7
Electrical conductivity at 25°C	6 × 10^{-8} recip. ohm
Evaporation rate of 95°F	
Minutes $\frac{1}{4}$	5%
Minutes $1\frac{1}{4}$	25%
Minutes $2\frac{3}{4}$	50%
Minutes $4\frac{1}{4}$	75%
Minutes $5\frac{1}{4}$	90%
Minutes $5\frac{1}{2}$	95%
Explosive limits	2.15–13.0%
Fire Point	18°C (0°F)
Flash point	−16°C
Freezing point	94.6°C
Heat of combustion	427 Cal./mole (7.373 Cal./g)
Heat of fusion	23.4 cal per g
Latent Heat of Vaporization at 56.1°C	124.5 Cal./g
Melting point	−95°C
Specific Gravity at 20/20°C	0.790–0.793
Specific Heat at 16°C	0.51 Cal./g
Refractive Index, N 20/D	1.3584
Surface tension at 20°C	23.7 dynes/sq cm
Solubility in water	Complete
Thermal conductivity	0.0004228 (liquid at 0°C)
Viscosity at 25°C	0.316 centipoise
Weight per gallon at 20°C	6.59 lbs.

Constant-boiling mixtures (% by wt.)			B.P.°C
Acetone 33	Carbon disulfide	67	39.3
77	Carbon tetrachloride	23	55.8
20	Chloroform	80	64.5
22	Diethyl amine	78	51.5
60	Ethyl iodide	40	55.5
73	Isobutyl chloride	27	55.8
55	Methyl acetate	45	56.1
88	Methyl alcohol	12	55.7

Acidity (as acetic)	0.002% by wt., max.
Distillation range at 760 mm	56.0–57.5°C
Non-volatile matter	1 mg. per 100 ml. (max.)
Purity	99%

Methyl Acetone (Methyl Ketone). Methyl acetone is a clear, colorless, flammable, volatile liquid, obtained from the product of the destructive distillation of wood. Although it varies in composition it is generally composed of acetone 35 to 60 per cent, methanol 20 to 40 per cent, and methyl

TABLE 13.2.—ACETONE-SOLUBLE PORTION OF CRUDE RUBBERS AND RELATED GUMS[6]

TYPE	PER CENT SOLUBLE AT BOILING POINT OF ACETONE
Balata, Surian sheet	41.9
Balata Venezuela block	44.5
Benguellas	4.5
Caucha, Ball	2.9
Caucha, Central	2.8
Crepe, brown	2.8
Crepe, first latex	2.9
Guayule	21.0
Gutta-percha	25.0
Smoked sheet, prime ribbed	3.15
Upper Congo, red	5.8
Upriver Fine Para	1.25

TABLE 13.3.—SOLUBILITY OF FATS, OILS AND GREASES IN ACETONE[6]

TYPE	MISCIBILITY AT 25°C	PER CENT SOLUBLE AT 25°C	PER CENT SOLUBLE AT BOILING POINT OF ACETONE
Linseed oil, ozonized	M		
Neatsfoot oil	m	98.7	M
Olive oil (commercial)	M		
Olive elaine (red oil)	M		
Palm oil, Legos (commercial)	m	82.0	99.8
Palm oil, raw		100.0	M
Palm kernel oil (extracted, raw)	M		
Peanut oil (refined and bleached)	M		
Peanut oil (hydrogenated)		100.0	M
Pine oil	M		
Seal oil (Norwegian, raw)	M		
Soy-bean oil	M		
Sperm oil	M		
Tallow (prime)		89.1	M
Whale oil	M		

M—miscible in all proportions.
m—part soluble at 25°C is miscible in all proportions.

TABLE 13.4.—SOLUBILITY OF BLOWN ASPHALTS IN ACETONE[6]

TYPE	ACETONE EXTRACT PER CENT
Residual oil	61.0
After blowing 3 hours	40.2
After blowing 6 hours	33.6
After blowing 8 hours	25.1

TABLE 13.5.—SOLUBILITY OF COPAL RESINS IN ACETONE[6]

TYPE	PER CENT SOLUBLE AT BOILING POINT OF ACETONE	SOLUBILITY OF PART SOLUBLE AT 25°C
Congo	40.8	M[1]
Manila, soft	96.6	M
Elemi	100.0	M
Yacca	96.6	M
Sandarac	97.0	M[1]
Sierra Leone	55.5	M[1]
Borneo pontianac	93.5	M[1]
Batavia dammar	88.7	M[1]
Red, accrodites	95.2	M

M—miscible in all proportions.
M[1]—miscible in concentrated solutions with separation on dilution.

TABLE 13.6.—SOLUBILITY OF WATER GUMS IN ACETONE[6]

TYPE	PER CENT SOLUBLE AT BOILING POINT OF ACETONE
Arabic gum	11.9
Indian gum	16.7
Senegal gum	12.0
Tragacanth, Allepa	9.2
Tragacanth, Persian	8.0
Tragacanth, Turkey	7.2

TABLE 13.7.—SOLUBILITY OF ASPHALTS AND BITUMENS IN ACETONE[6]

TYPE	PER CENT SOLUBLE AT BOILING POINT OF ACETONE
Alberite	5.8
Asphalt, blown, from mid-continental petroleum	56.4
Bermudez pitch, refined	62.4
Coal-tar pitch, refined	70.4
Fatty acid pitch, soft grade	62.4
Fatty acid pitch, medium grade	54.3
Gilsonite selex	25.0
Grahamite	1.6
Mexican petroleum asphalt, steam-distilled, medium grade	44.2
Mexican petroleum asphalt, steam-distilled, soft grade	64.3
Petroleum asphalt, steam-distilled, California, medium grade	81.0
Residual oil from Gulf Coast	61.0
Residual oil from steam distillation of mid-continental petroleum asphalt	97.2
Syrian asphalt	5.9
Trinidad pitch, refined	42.0

TABLE 13.8.—SOLUBILITY OF SHELLACS IN ACETONE[6]

TYPE	PER CENT SOLUBLE AT BOILING POINT OF ACETONE
Superfine orange shellac	98.8
Superfine shellac	92.8
T. N. shellac, No. 1	95.6
T. N. shellac, No. 2	98.8
A. C. garnet	81.3
Refus lac	63.0

TABLE 13.9.—PERCENTAGE OF ACETONE-INSOLUBLE MATTER IN VARIOUS RESINS[6]

TYPE	PER CENT INSOLUBLE IN ACETONE
Kauri, pale	8.90
Kauri, brown	38.70
Kauri, bush	20.70
Rosin	Soluble
Burgundy pitch	Soluble
Stockholm tar	Soluble
Mastic	9.50
Sandarac	Soluble
Madagascar copal, fused	84.80

TABLE 13.10.—SOLUBILITY OF FATS, OILS AND GREASES IN ACETONE[6]

TYPE	MISCIBILITY A 25°C.	PER CENT SOLUBLE AT 25°C.	SOLUBILITY AT BOILING POINT OF ACETONE
Chinawood oil	M		
Coconut oil (refined and bleached)	M		
Corn oil (raw)	M		
Cottonseed oil (refined and bleached)	M		
Cottonseed oil (hydrogenated, Crisco)	M	100.0	M
Cottonseed oil (hydrogenated)		32.0	M
Cottonseed oil (stearin)	M		
Cottonseed oil (summer)	M		
Cottonseed oil (winter)	M		
Fish oil (herring, raw)	M		
Fish oil (hydrogenated)		35.8	M
Fish oil (menhaden, raw)	m	99.8	M
Grease, brown	m	96.4	99.8
Grease, garbage	m	99.6	99.7
Grease, white	m	97.3	M
Linseed oil, raw	M		

M—miscible in all proportions.

m—part soluble at 25°C is miscible in all proportions.

Table 13.11.—Solubility of Waxes in Acetone[6]

Type	Per cent soluble at boiling point of acetone
Bayberry wax	100.0
Beeswax, African	93.9
Beeswax, Cuban	99.2
Candelilla wax	99.8
Carnauba wax, Flora	35.8
Carnauba wax, Ceara	48.8
Japan wax	100.0
Montan wax	62.5
Ozocerite, black	69.0
Shellac wax	58.8

acetate 20 to 30 per cent. One manufacturer[7] offers a synthetic methyl acetone which contains 47.5 to 51 per cent of acetone, 20 to 25 per cent of methanol, and 27.5 to 31 per cent of methyl acetate. This mixture is miscible with water, oils and hydrocarbons in all proportions and is an excellent solvent for nitrocellulose and cellulose acetate, benzyl abietate, ester gum, glyptal resins, gums, resins, etc. It is used to a large extent in the manufacture of lacquers. Other uses are as an ingredient in paint and varnish removers; in the manufacture of celluloid cements, extracts, artificial leather, gas mantles, and rubberized fabrics; in the extraction of perfumes; as a solvent for alcohol-soluble gums and gum mixtures, dopes, enamels, and stains, solidified alcohol, and plastics; as a dewaxing agent for dammar and other natural gums, etc.

Acidity	0.02% max.
Boiling range	50–70°C
Specific gravity at 20/20°C	0.829–0.835
Weight per gallon at 20°C	7.0

Methyl Ethyl Ketone (Butanone-2, Ethyl Methyl Ketone) ($CH_3—CO—C_2H_5$). A colorless, stable, mobile, flammable liquid with an odor like acetone, methyl ethyl ketone was originally found in a mixture called "light acetone oil", a by-product of the wood distillation industry; it is now made synthetically from *sec* butanol. Its production has grown steadily to a production of 75 million pounds a year. It is completely miscible with most organic solvents and will dissolve many natural and synthetic resins and gums such as kauri, manila, pontianac, copal, coumarone, camphor, dammar and the amberol, glyptal and vinyl type resins. Generally it is equivalent to acetone in solvent power, with the additional advantages of being less soluble in water, having both a higher boiling point and a lower vapor pressure and thus a lesser tendency to cause "chilling".

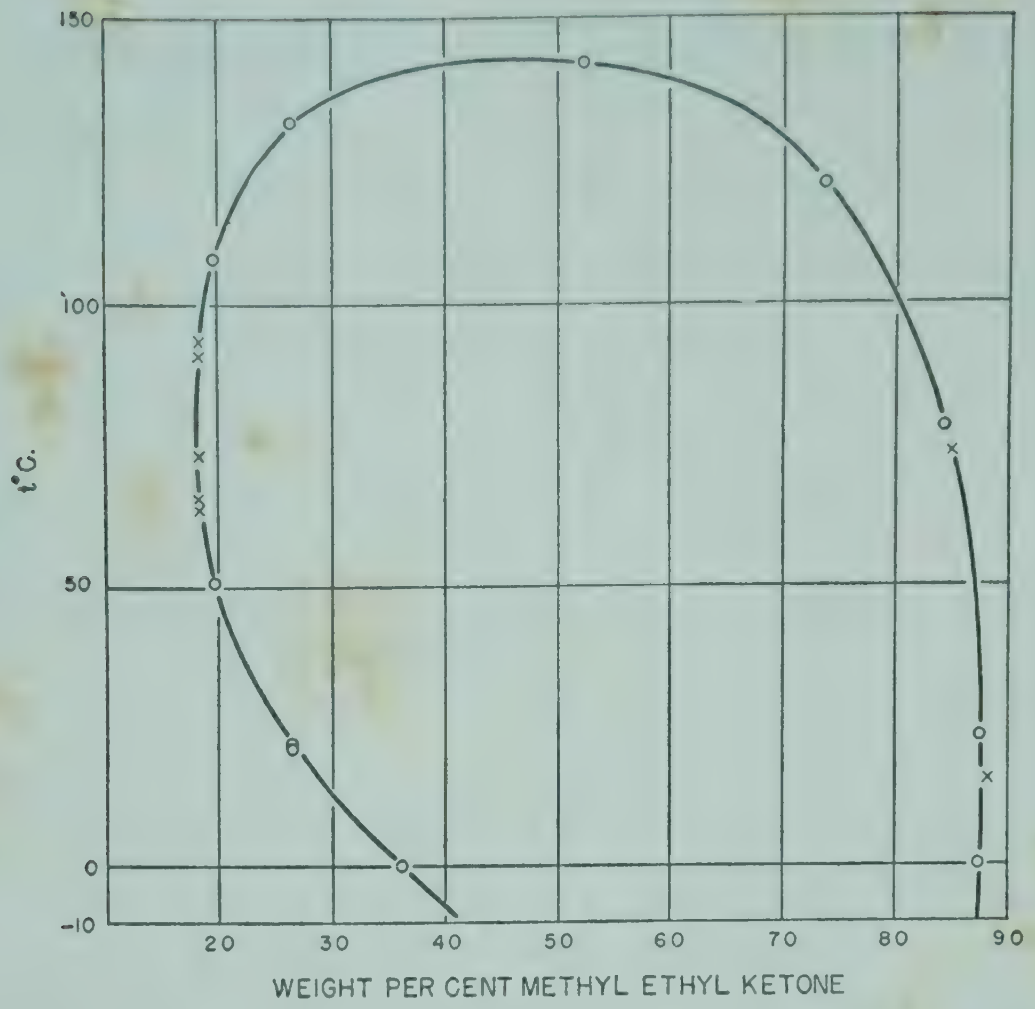


FIGURE 13.9. Solubility of Methyl Ethyl Ketone in Water.[3]
○—Shell Development Company
×—Marshall, J. Chem. Soc. 89, 1381 (1906)

Methyl ethyl ketone is a solvent for nitrocellulose; its presence in lacquers lowers the viscosity and permits the addition of more solids. It is a good solvent for the vinyl resins and its powerful solvent action is made use of in paint and varnish removers, as a cleanser for metal surfaces, in dyeing[8], and in the refining of mineral oils[9], and dewaxing of lubricating oils. It is an extraction medium for fats, oils, natural resins, and waxes. It is used in the manufacture of celluloid, artificial leather, dopes and dyes. It has been shown to have the same solvent action for certain rubber fractions that is exhibited by chloroform[10], and is a solvent for natural and synthetic antioxidents.[11] It forms a constant-boiling mixture having 88.7 per cent by weight of methyl ethyl ketone and 11.3 per cent by weight of water. This mixture has a boiling point of 73.4°C, a refractive index of 1.37700, and a density from 0.8342 to 0.8358. It can be dehydrated by allowing it to percolate through a bed of rock salt. In this process two layers are formed, of which the upper is composed of methyl ethyl ketone with a small amount of water. When distilled, this upper layer becomes anhydrous.

Work has been done on other combinations of pairs to determine whether they will form azeotropic mixtures with methyl ethyl ketone. These pairs are ethyl alcohol and carbon tetrachloride, ethyl alcohol and carbon disulfide, ethyl alcohol and methyl propionate, ethyl alcohol and benzene ethyl alcohol and cyclohexane, carbon tetrachloride and methyl propionate, and carbon tetrachloride and cyclohexane. The results, however, have proved that these are nonazeotropic.

Azeotropic Mixtures

	% by wt.		% by wt.	B.P. (°C)
Methyl ethyl ketone	37.5	Benzene	62.5	78.4
	73	*tert*-Butyl alcohol	27	77.5
	84.7	Carbon disulfide	15.3	45.9
	29	Carbon tetrachloride	71	73.8
	40	1,3-Cyclohexadiene	60	73.0
	40	Cyclohexane	60	72.0
	12	Ethyl acetate	82	77.0
	60	Ethyl alcohol	40	74.8
	20	Ethyl sulfide	80	77.5
	70	Isopropyl alcohol	30	77.5
	52	Methyl propionate	48	79.3
	55	Propyl formate	45	79.5
	75	Propyl mercaptan	25	55.5
	45	Thiophene	55	76

Ternary Mixtures

						B.P. (°C)
(1) Methyl ethyl ketone	22.2	Water	3.0	CCL$_4$	74.8	65.7
(2)	17.8		8.9	C_6H_6	73.8	68.9
Upper layer of (2)	19.0		0.4		80.6	
Lower layer of (2)	3.5		96.4		0.1	

Typical Properties and Specifications

Boiling point at 760 mm	79.6°C
Coefficient of expansion	0.00076 per °F
Electrical Conductivity	1.0×10^{-7} ohms at 25°C
Explosive limits	1.97%—10.2%
Flash point (Tag Closed Cup)	25°F
Freezing point	−86.4°C
Heat of combustion	582 Cal./mole
Latent heat of Vaporization at 20°C	106.0 cal./g
Refractive Index, N 20/D	1.3788
Solubility of water in solvent	23.4% by wt.
Specific gravity at 20/20°C	0.805–0.807
Specific heat	0.55 cal./g
Surface tension	
0°C 26.9 dynes/sq cm	
20 24.6	
40 22.3	
75 18.4	
Viscosity at 15°C	0.00423 poise
Weight per gallon at 20°C	6.72 lbs.
Acidity (as acetic)	0.0025 by wt. (max.)
Distillation range (ASTM)	70°–80.5°C
Non-volatile matter	3 mg. per 100 ml. (max.)
Purity	99%

Viscosity of Methyl Ethyl Ketone[3]

Temp. (°C)	Poise
0.32	0.005361
7.04	.004923
14.10	.004522
21.31	.004170
28.36	.003861
35.42	.003586
42.49	.003342
48.72	.003149
55.92	.002944
63.74	.002750
70.26	.002595
76.25	.002465

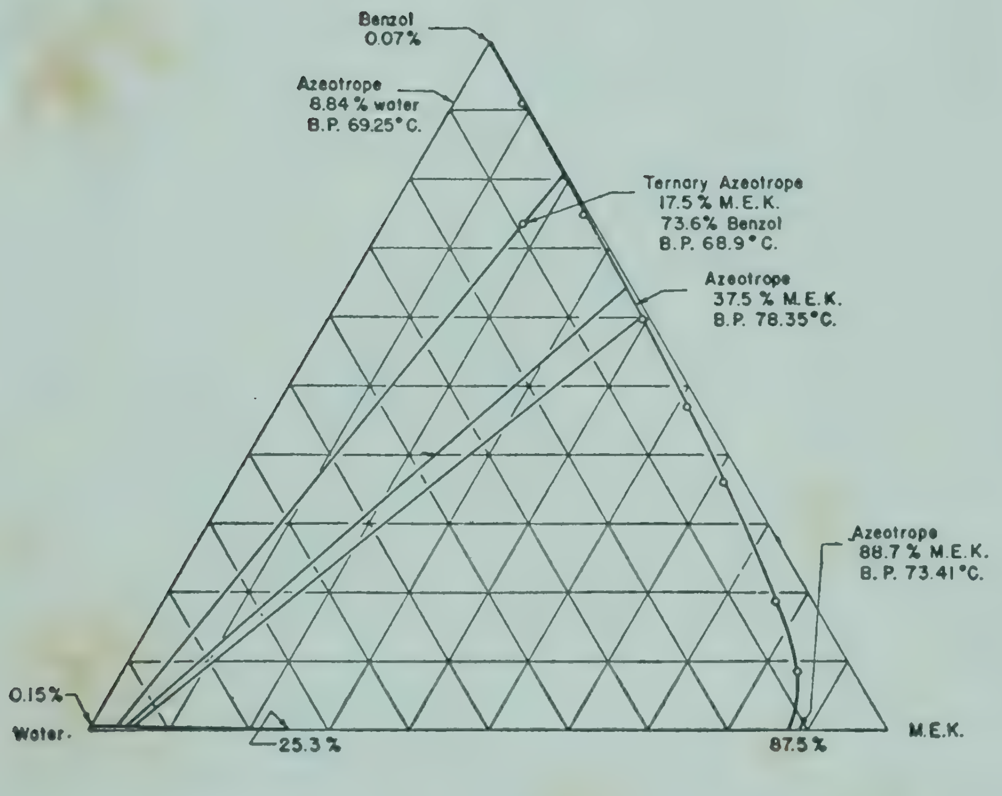


FIGURE 13.10. System: Methyl Ethyl Ketone-Benzol-Water at 25°C.[3]

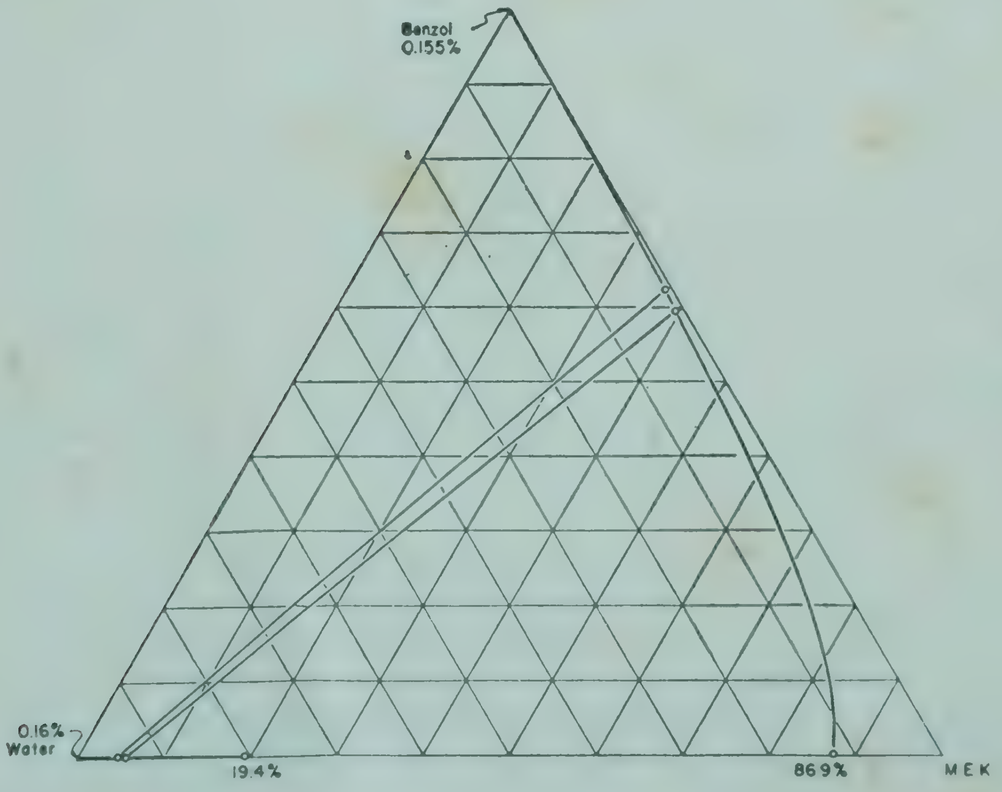
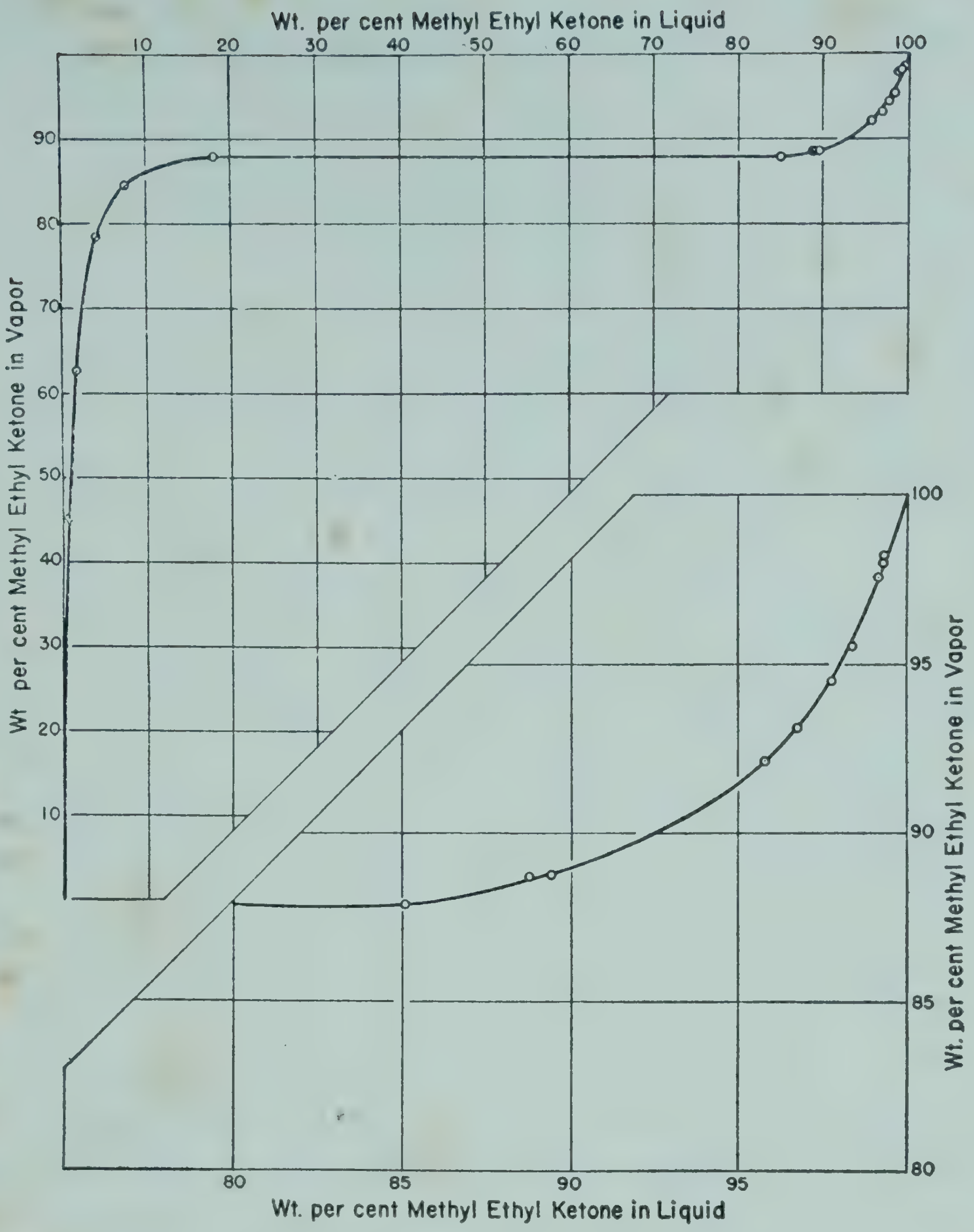


FIGURE 13.11. System Methyl Ethyl Ketone-Benzol-Water at 50°C.[3]



Vapor and Liquid Composition at the Boiling Point

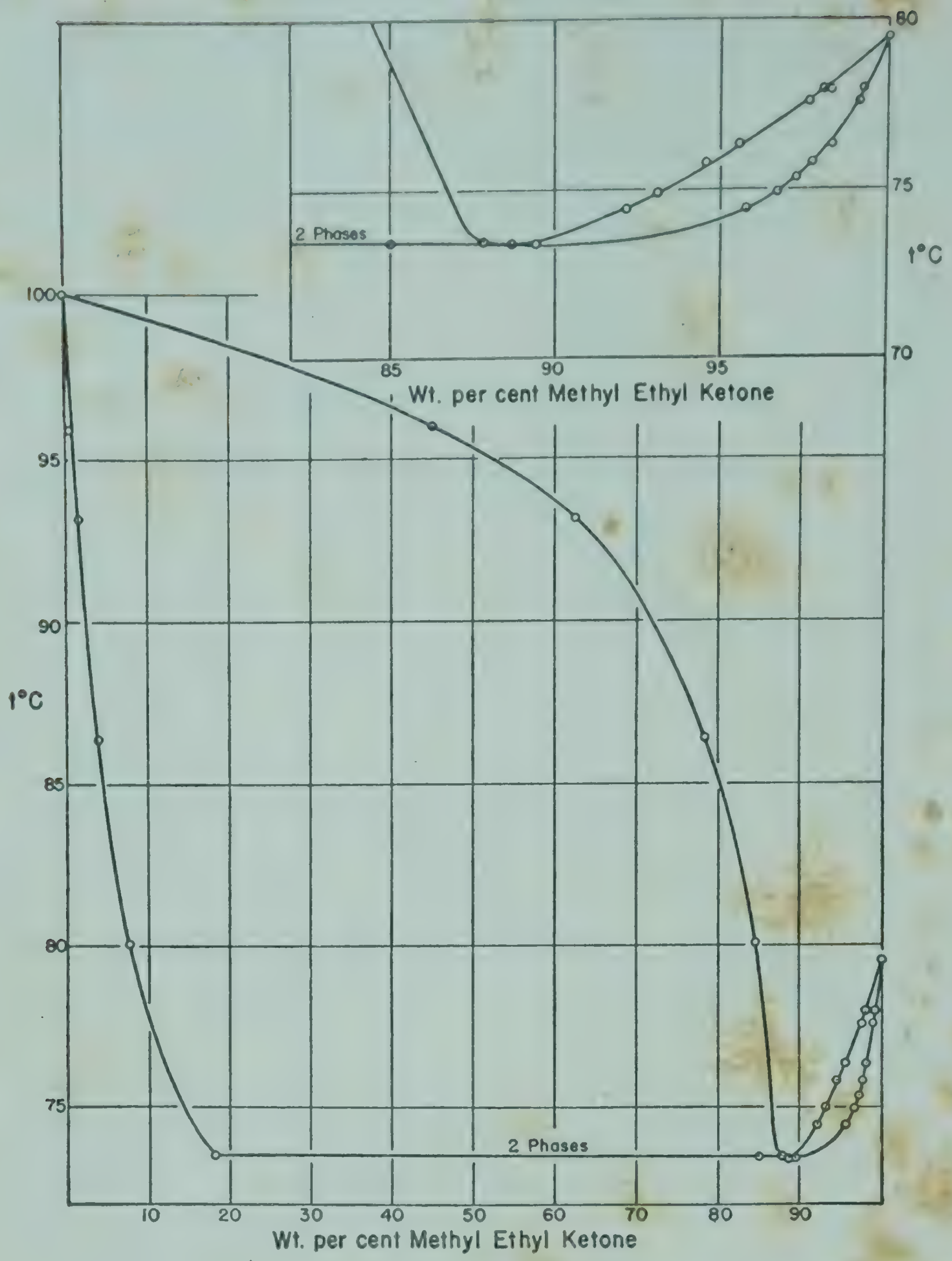
Pressure = 1 Atm.

FIGURE 13.12. Methyl Ethyl Ketone and Water.[3]

Methyl *n*-Propyl Ketone (Pentanone-2) ($CH_3 \cdot CO \cdot CH_2 \cdot C_2H_5$). Commercial Methyl *n*-propyl ketone, produced synthetically by dehydrogenation of the corresponding alcohol, consists of a mixture of methyl *n*-propyl and diethyl ketones in the approximate ratio of 3 to 1, and contains at least 97% of these ketones, the balance being secondary amyl alcohol. It is a colorless liquid, soluble in alcohol and ether but only very slightly soluble in water.

Typical Properties and Specifications

Boiling point	101.7°C
Dielectric constant	15.4
Flash point (closed cup)	7.2°C
Latent heat	91 cal./g
Freezing point	−77.8°C



Vapor and Liquid Compositions at the Boiling Point

Pressure = 1 Atm.

FIGURE 13.13. Methyl Ethyl Ketone and Water.[3]

Specific gravity at 20/20°C	0.809
Refractive index at 20°C	1.3895
Surface tension at 20°C	25.2 dynes/cm.
Vapor pressure at 20°C	30 mm. Hg
Viscosity at 25°C	0.473 centipoise
Water Tolerance at 20°C	Miscible without turbidity with 19 volumes of 60° Bé gasoline
Acidity (as acetic acid)	0.003% by wt., max.
Distillation range	More than 90% distills over between 100 and 103°C
Non-volatile matter	0.005% max.

Methyl n-Butyl Ketone (Hexanone-2) ($CH_3 \cdot CO \cdot C_4H_9$). Methyl n-buty ketone is a colorless liquid, freely soluble in alcohol and ether but ver slightly soluble in water.

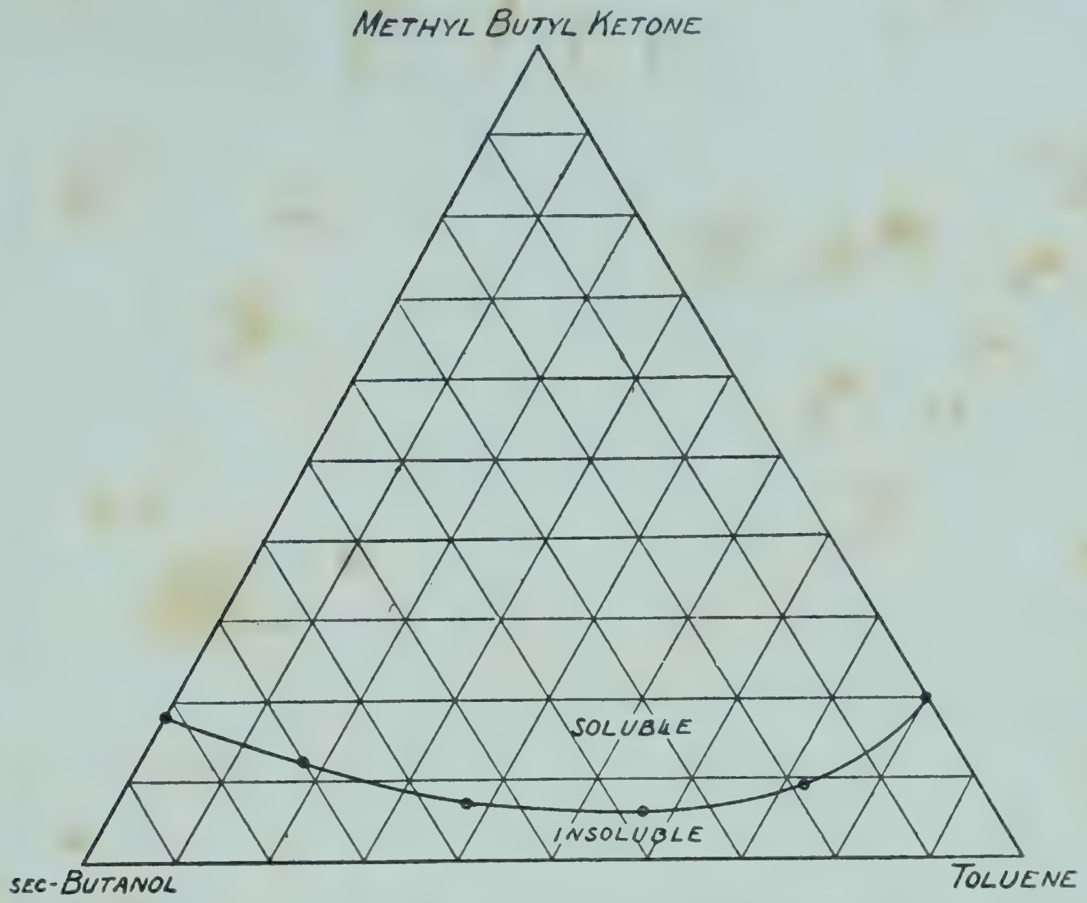


FIGURE 13.14. Solubility of Dry Half-Second R. S. Nitrocellulose in a System of Methyl Butyl Ketone-*sec*-Butanol-Toluene.[4]

Typical Properties and Specifications

Boiling point at 760 mm	127.2°C
Dielectric constant	12.2
Flash point (closed cup)	22.8°C
Latent heat	83 cal./g
Freezing point	−56.9°C
Specific Gravity at 20/4°C	0.8209
Refractive index at 20°C	1.4024
Specific heat	0.553 cal./g
Surface tension at 20°C	25.2 dynes/sq cm
Vapor pressure at 20°C	10 mm. Hg
Viscosity at 25°C	0.584 centipoise

Methyl Isobutyl Ketone (Hexone, 4-Methylpentanone-2,2-Methyl-4-pentanone) ($CH_3\cdot CO\cdot C_4H_9$). Although first prepared in 1849 methyl isobutyl ketone was not made synthetically and on a large scale until the last decade. It is a stable, colorless liquid classified as a medium boiler. It is miscible with most organic solvents and with mineral and vegetable oils. When compared with butyl acetate its rate of evaporation is somewhat faster so that it can either replace esters or be combined with them. Its rate of evaporation is somewhat faster than that of butyl acetate. It is used in the vinyl type resins for coatings where it helps to prevent gelling and lowers viscosity, in nitrocellulose lacquer manufacture, in extraction processes and in chemical synthesis. It may be used in dewaxing oils and

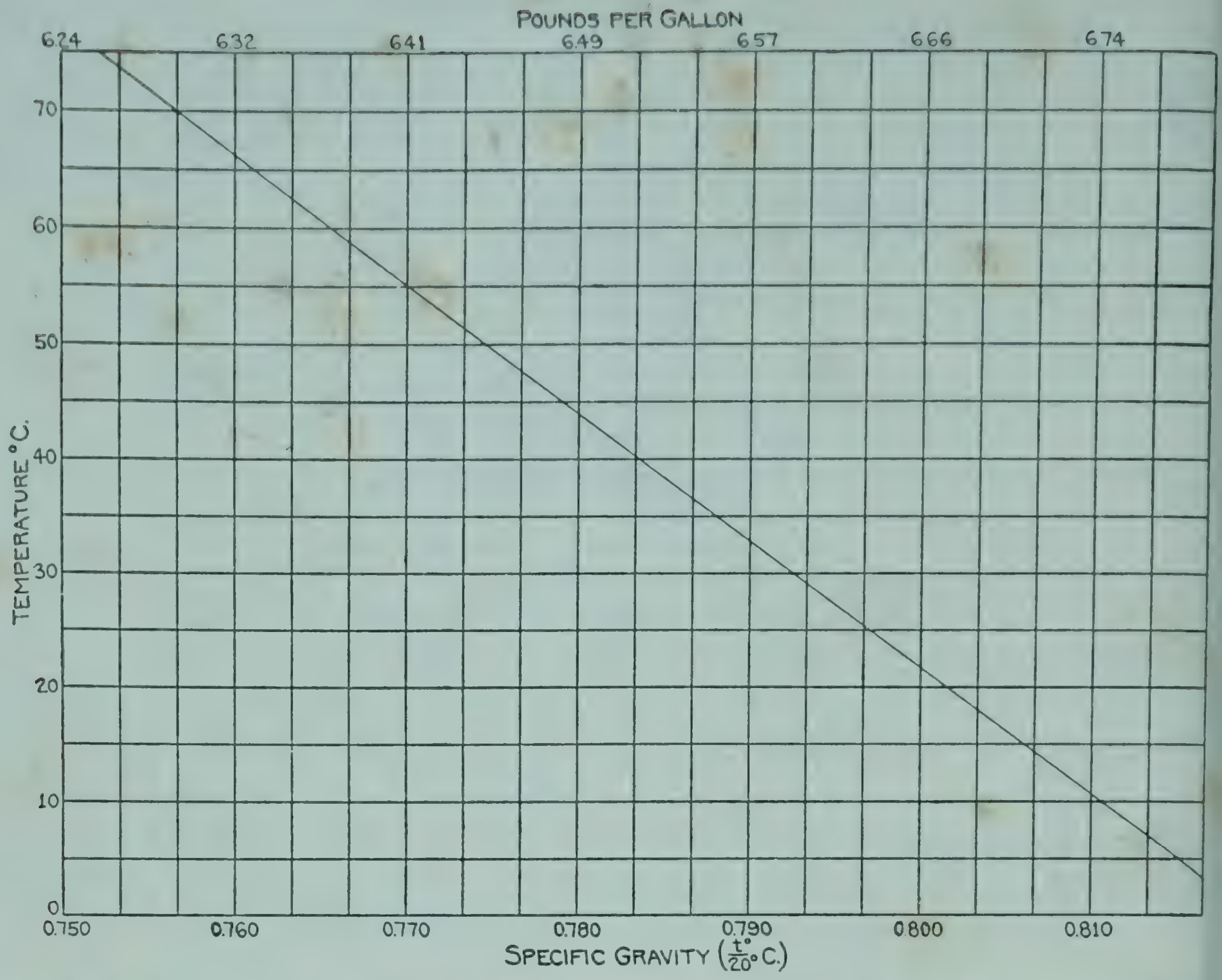


FIGURE 13.15. Specific Gravity and Weight per Gallon of Methyl Isobutyl Keton at Various Temperatures.[7]

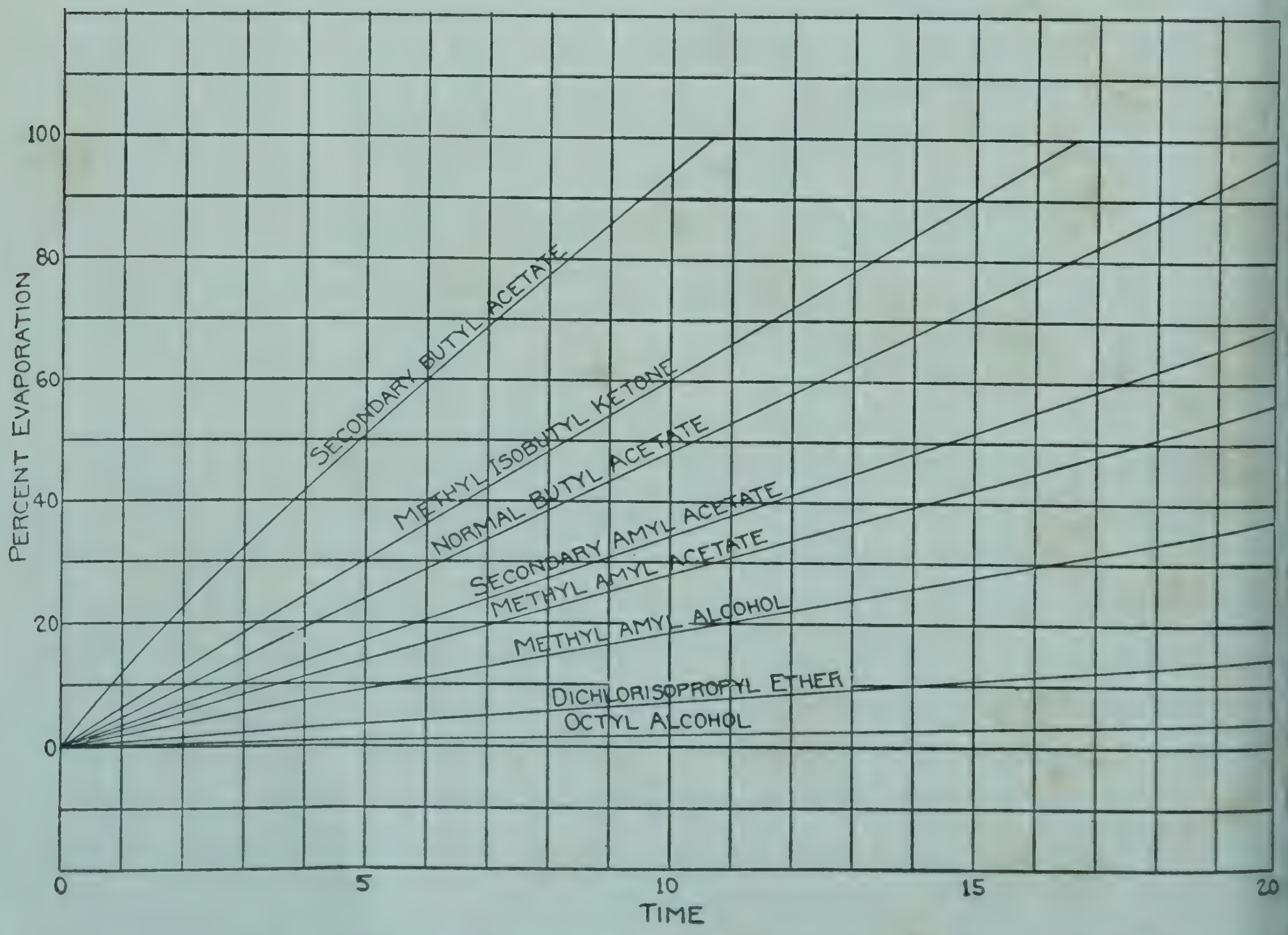


FIGURE 13.16. Evaporation Rate of Various Solvents at Room Temperature.[7]

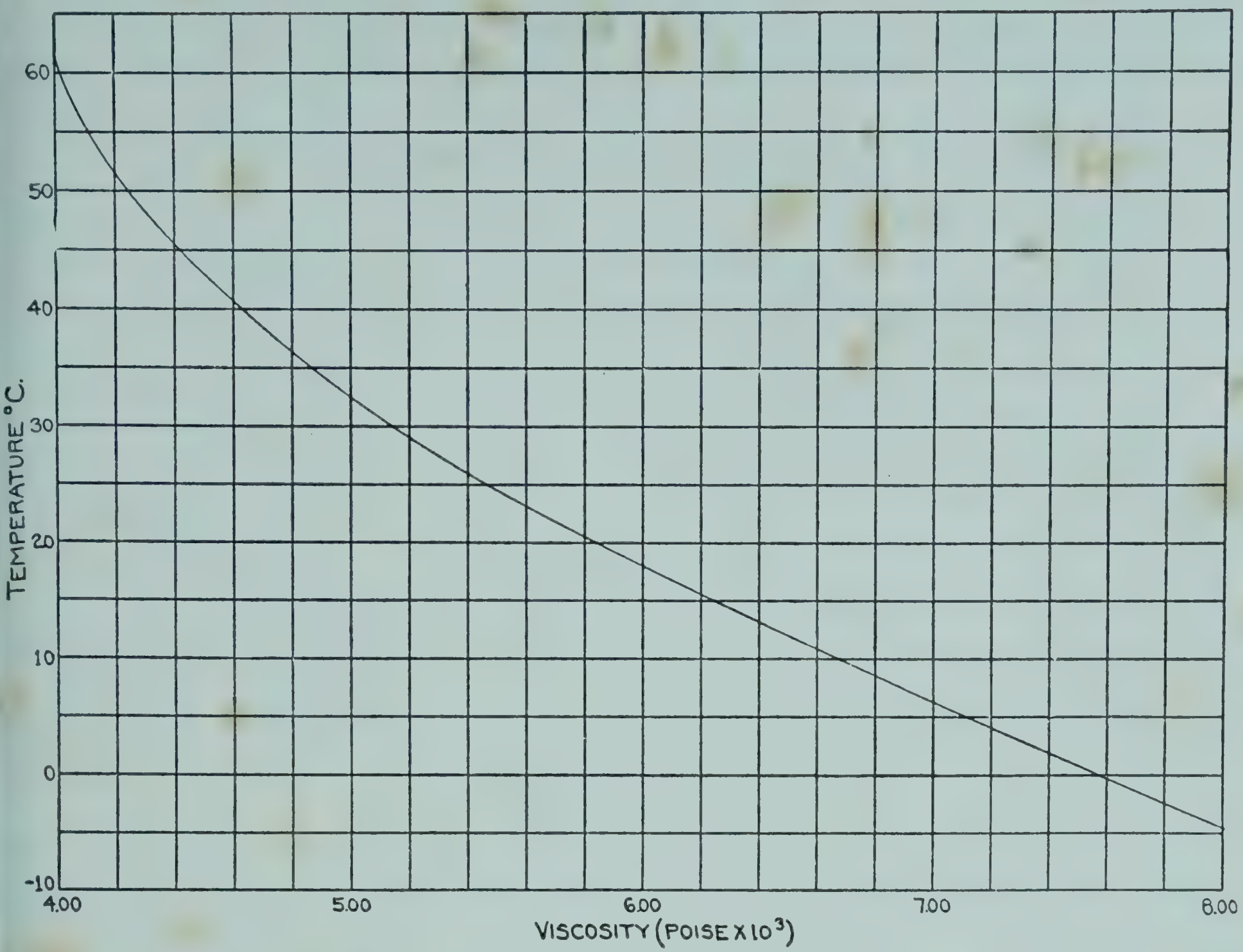


FIGURE 13.17. Viscosity of Methyl Isobutyl Ketone at Various Temperatures.[7]

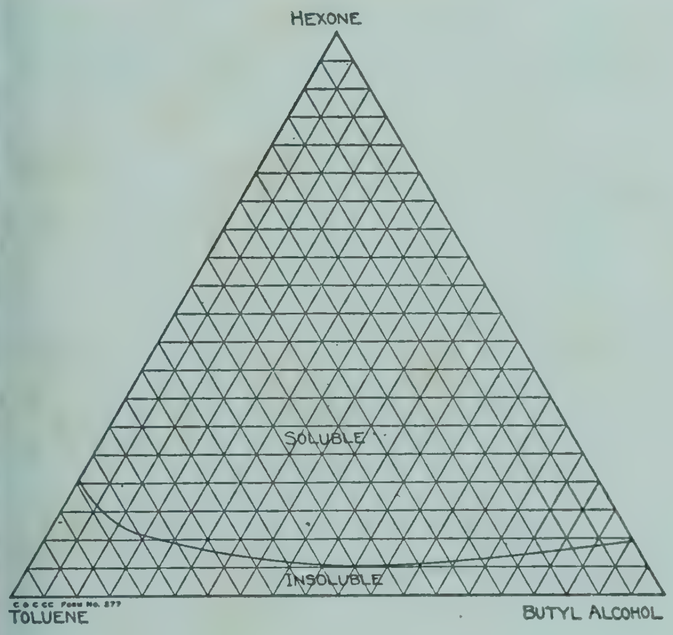


FIGURE 13.18.
Solubility of ½-Sec. R. S. Nitrocellulose in Mixtures of Methyl Isobutyl Ketone, Butyl Alcohol and Toluene.[7]

in paint removers. Table 13.12 gives the solubility of various substances in methyl isobutyl ketone.

Typical Properties and Specifications

Boiling point at 760 mm	115.9°C
Coefficient of expansion	0.000625 per °F
Color	Water-white
Dilution ratio	Kemsolene = 1.1 Toluene = 3.5 Final conc. ½ sec. R.S. Nitrocellulose 8%

Evaporation rate (*n*-butyl acetate = 1.00)	1.5
Flash point (Tag closed cup)	60°F
Freezing point	−84.7°C
Heat of combustion	8910 cal./g
Latent Heat of Vaporization	87 cal./g
Solubility in water at 20°C	1.91% by wt.
Solubility of water in Ketone at 20°C	2.81% by wt.
Specific gravity at 20/20°C	0.799 to 0.804
Specific heat at 20°C	0.46 cal./g
Refractive Index, N 20/D	1.3958
Surface tension at 25°C	25.4 dynes/sq cm
Viscosity at 25°C	0.00546 poise
Water tolerance	Viscible without turbidity with 19 vols. of 60° Bé gasoline at 20°C
Weight per gallon at 20°C	6.68 lbs.
Acidity (as acetic)	0.02% by wt., max.
Distillation range (ASTM)	114–117°C
Purity	99% min

HEPTANONES

Methyl *n*-Amyl Ketone (Heptanone-2) [$CH_3(CH_2)_4 \cdot CO \cdot CH_3$]. This ketone is a colorless, stable liquid, miscible with most lacquer solvents and only very slightly soluble in water. It is used as a high-boiling solvent for nitrocellulose and is particularly applicable in vinyl resin finishes, where its slow rate of evaporation prevents quick drying, improves the flow and gives blush resistance; also used with some effect in insecticidal preparations.

Typical Properties and Specifications

Boiling point	151°C
Color	Water-white
Dilution Ratio (toluene)	3.9
Dryness	Miscible with 19 vol. Bé. gasoline at 20°C
Flash point (closed cup)	106°F
Latent heat of vaporization	83 cal./g
Specific Gravity at 20/20°C	0.816 to 0.821
Refractive Index at 20°C	1.4110
Vapor pressure at 20°C	3.6 mm. Hg
Viscosity at 25° C	0.766 centipoise
Weight per gallon at 20°C	6.81 lbs.
Acidity (as acetic)	0.5% by wt., max.
Boiling range at 760 mm	
Below 147°C	None
Below 149	Not more than 5%
Below 152	Not less than 95%
Above 154	None
Non-volatile matter	0.005 g per 100 cc max.
Purity	95% min.

Table 13.12.—Solubility of Miscellaneous Materials in Methyl Isobutyl Ketone at 20°–25°C[3]

Soluble, Over 5% by Weight Concentration

Acid
  Oleic (Technical Red Oil)

Oils
  Castor, Refined Raw
  Cottonseed, Raw
  China Wood
  Coconut, Crude
  Fish, Processed
  Linseed, Pure Raw
  Mineral, 70/80 viscosity
  Pine
  Soybean, 2–3 viscosity

Gums
  Elemi
  Kauri (Pale Bold)
  Mastic
  Pontianak

Resins, Natural
  Dammar (dewaxed)
    Batavia
    Singapore
    Light Rosin
  Sandarac

RESINS, SYNTHETIC*

Trade Name	Type
Amberlac 80-X	Modified drying type phthalic alkyd
Amberol 801	Rosin modified maleic alkyd
Arochem 519	Modified maleic
Aroclor 1260	Chlorinated diphenyl
Bakelite BR-254	Non-heat-hardening 100% para-phenylphenol resin
No. 1 Solid Beckosol	Phenolic modified drying type alkyd
Beckosol 1313	Drying type alkyd
Beetle 227–8	Unmodified urea-formaldehyde
Cellolyn 102	Modified rosin ester
Ester gum	Rosin ester
Ethyl methacrylate	Acrylic ester
Glyptal 2477	Non-drying type alkyd
Melmac 245-8	Unmodified melamine-formaldehyde
Neville R-21 (soft)	Unmodified coumarone-indene
Nevillite 1	Naphthene polymers
Nitrocellulose	Cellulose ester
Parlon X (20 cps.)	Chlorinated rubber
Phenac 608	Modified phenolic
Santolite K	Alkyl-arylsulfonamide-formaldehyde
Saran F–120	Vinylidenechloride-acrylonitrilecopolymers
Staybelite	Hydrogenated rosin ester
Teglac Z-152	Rosin modified maleic alkyd
Vinylite AYAF	Polyvinyl acetate
Vinylite VMCH	Maleic modified vinyl chloride-vinyl acetate copolymers
Vinylite VYHH	Vinyl chloride-vinyl acetate copolymers

TABLE 13.12.—*Continued*

Soluble, Less than 5% by Weight Concentration

Acids	Asphalts
Lanolin, USP	Air Blown, 150°F.
Stearic, TP	Paving, 51/60 Penetration
Gums	Resins, Natural
Chips, Pale East India	Dammar (dewaxed)
Congo, East India	Black East India
Congo, Pale Cracked	Borneo
Kauri, Brown	Pale Bold East India
Kauri, White	Helix Wood
Philippine Manila	Shellac, Orange

RESINS, SYNTHETIC*

Trade Name	Type
Ethocel (10 cps.)	Cellulose ether
Methyl methacrylate	Acrylic ester
Raw neoprene	Chloroprene polymers
Styron VA	Polystyrene

Insoluble

RESINS, SYNTHETIC*

Trade Name	Type
Benzyl cellulose	Cellulose ether
Cellulose acetate	Cellulose ester
Cellulose acetate butyrate	Cellulose mixed ester
Cellulose triacetate	Cellulose ester
Ethocel (15 cps.)	Cellulose ether
Formvar "E"	Polyvinyl formal
Geon 101	Polyvinyl chloride
Geon 202	Vinyl chloride-vinylidene chloride copolymers
Vinylite XYHL	Polyvinyl butyral

* Methyl isobutyl ketone should exhibit similar solvency for resins of the same general type although these may be offered under trade names other than those listed above.

Ethyl Butyl Ketone (Heptanone-3) ($C_2H_5COCH_2CH_2CH_2CH_3$). Ethyl butyl ketone[7] is a stable, high-boiling solvent of special value in lacquers and synthetic resin coatings. Its evaporation rate in relation to those of comparable solvents is indicated in the following tabulation:

Solvent	Hours
Methyl isobutyl ketone	4.5
Butyl acetate	8
Ethyl butyl ketone	14
Amyl acetate	16
Methyl amyl acetate	17
Methyl amyl ketone	20
"Cellusolve" acetate	38
Diisobutyl ketone	44

The unusual combination of good solvent power with medium evaporation rate makes ethyl butyl ketone generally useful for coating solutions having adequate flow without unduly long drying time. It bakes out of films somewhat faster than other comparable ketones. Solution viscosities of "Vinylite" resin VYHH in ethyl butyl ketone and methyl amyl ketone are as follows:

	10% solids	15% solids	20% solids
Ethyl butyl ketone	16.6 sec.	25.0 sec.	58.8 sec.
Methyl amyl ketone	17.2 sec.	25.0 sec.	62.0 sec.

Ethyl butyl ketone is useful in solvent mixtures for both air-dried and baked finishes based on nitrocellulose or the vinyl resins. Its good solvent power and medium evaporation rate make ethyl butyl ketone of interest for preparing "Vinylite" resin solutions having adequate flow-out without an unduly long drying time. Ethyl butyl ketone is particularly useful in formulating organosals based on "Vinylite" resin VYNV and is used for adjusting the volatility of the dispersant in organosals in which the volatility of diisobutyl ketone is too low.

Boiling point	147.8°C
Freezing point	−36.7°C
Coefficient of expansion at 20°C	0.00107
Flash point	125°F
Solubility in water at 20°C	0.43% by wt.
Sollubility of water in at 20°C	0.78% by wt.
Refractive index at 20°C	1.4085
Specific gravity at 20/20°C	0.8197

Di-*n*-Propyl Ketone (Heptanone-4, butyrone, amyl ketone) [$(CH_3\,CH_2\text{-}CH_2)_2CO$]. Di-*n*-propyl ketone is a colorless, stable liquid having a pleasant odor. It is miscible with many organic solvents, and dissolves a wide variety of materials, some of which are crude rubber, nitrocellulose, raw and blown oils, many natural and synthetic resins like dewaxed dammar, manila, rosin, cumar, ester gum, glyptals and waxes. Its most important use is as a solvent in lacquers and synthetic resin finishes. It is also used in chemical synthesis.

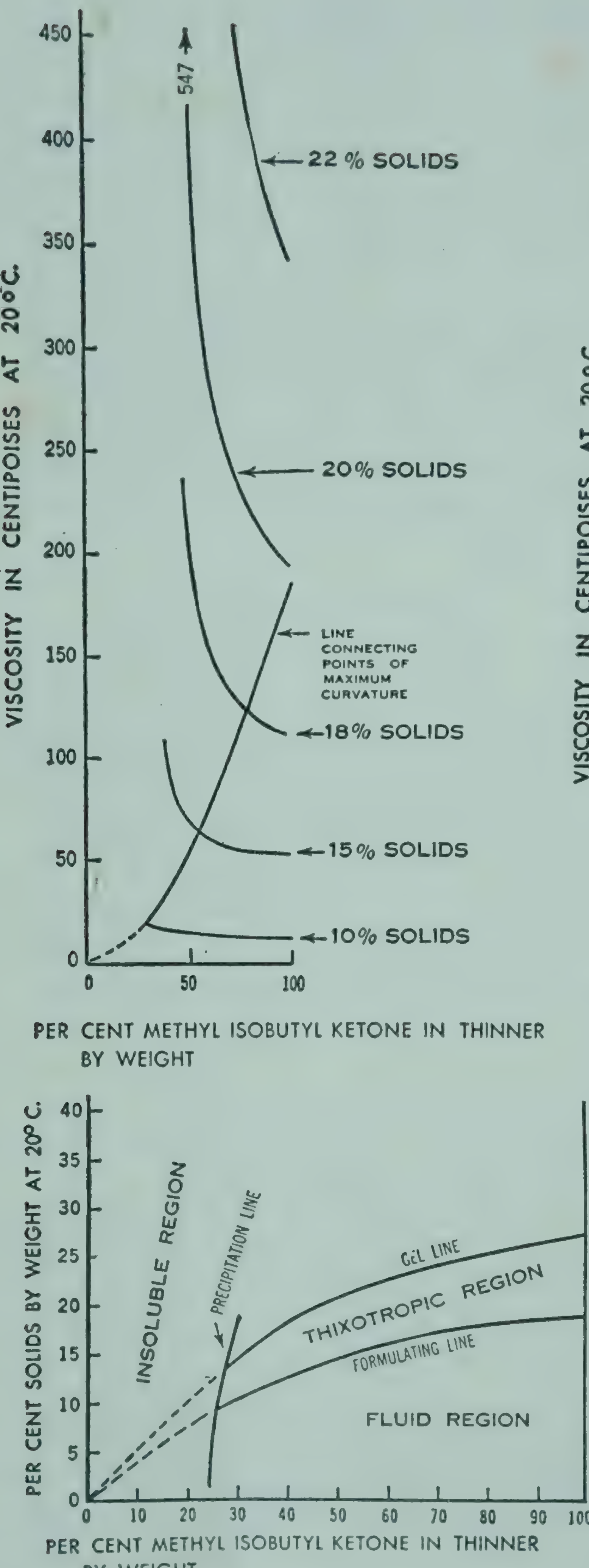


FIGURE 13.19. Equilibrium Viscosities and Phase Diagram of Resin VYHH in Methyl Isobutyl Ketone-Solvesso No. 1 Mixtures.

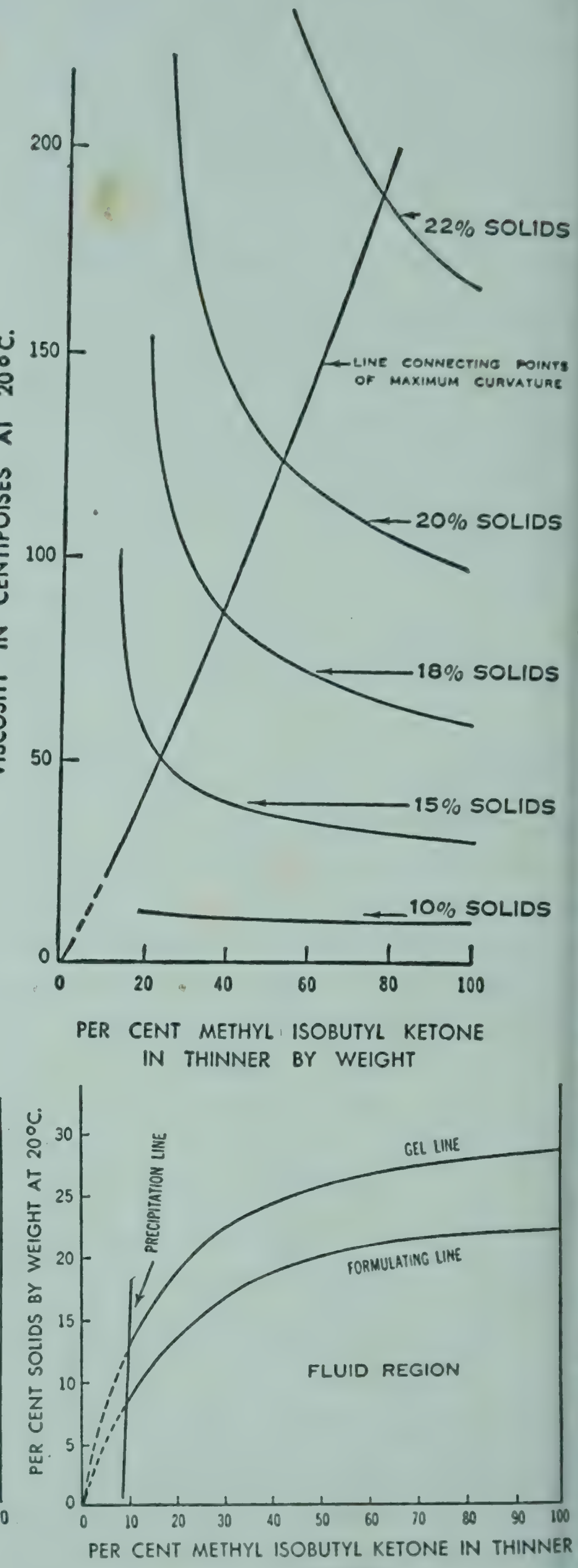


FIGURE 13.20. Equilibrium Viscosities and Phase Diagram of 3:2 Resin VYHH-VYLF Mixtures in Methyl Isobutyl Ketone-Toluene Thinners.

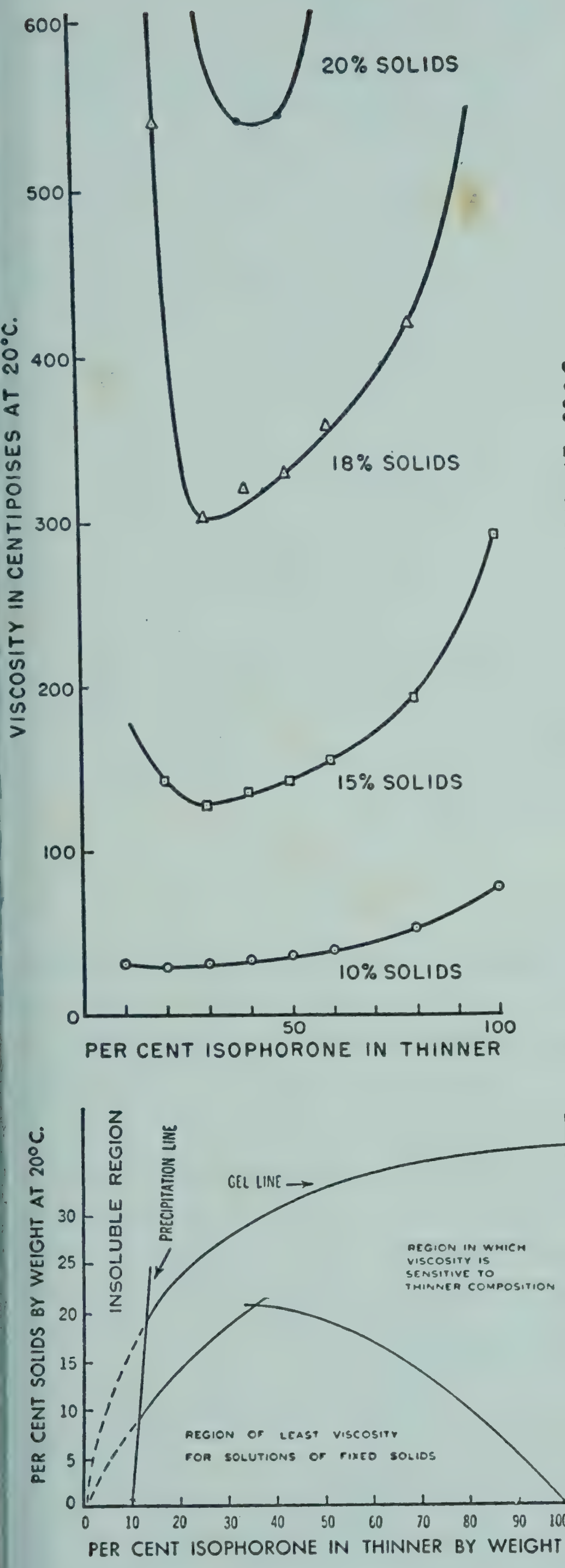


FIGURE 13.21. Equilibrium Viscosities and Phase Diagram of Resin VYHH In Isophorone-Xylene Mixtures.

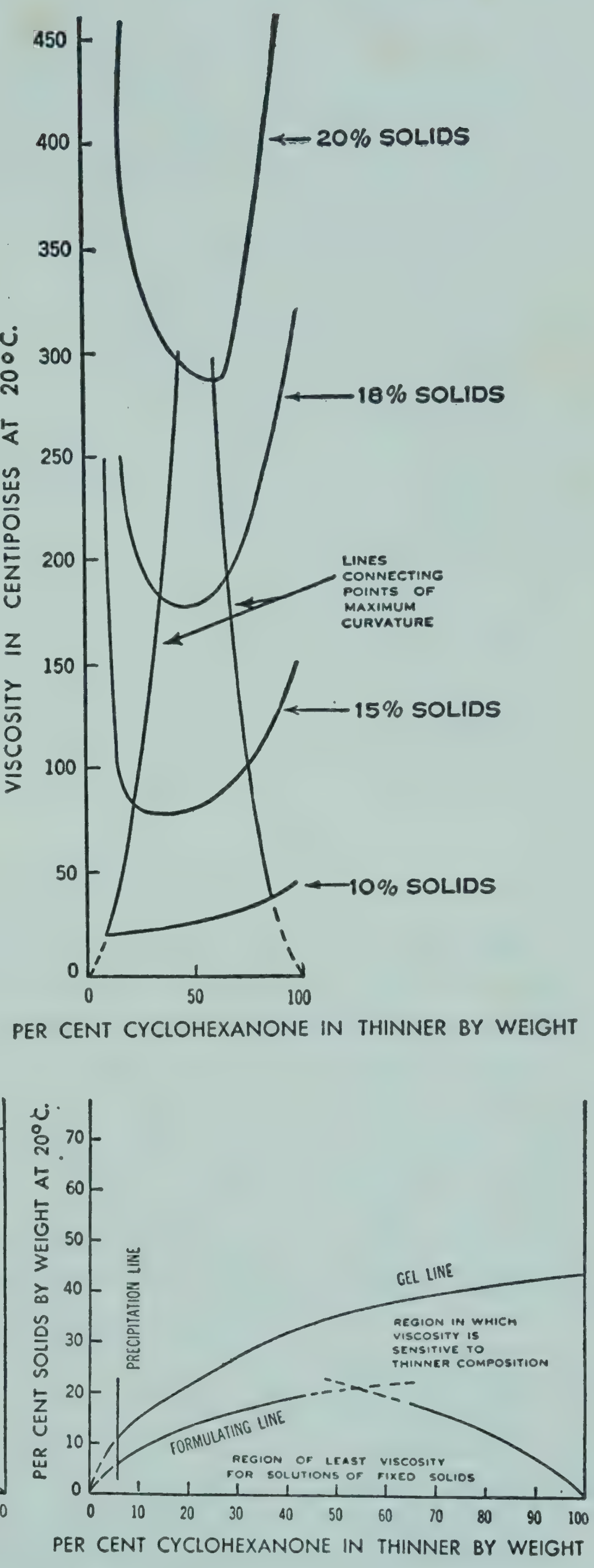


FIGURE 13.22. Equilibrium Viscosities and Phase Diagram of Resin VYHH in Cyclohexanone-Toluene Mixtures.

Typical Properties and Specifications

Boiling point	143.7°C
Coefficient of expansion	0.001073 (per °C) to 20°C 0.001115 (per °C) to 55°C
Dilution ratio (Kemsolene)	0.8
(Toluene)	3.1
Flash point (ASTM Open Cup)	49°C
Freezing point	−32.1°C
Heat of combustion	1051 cal./mole
Latent heat of vaporization	75.8 cal./g
Solubility in water at 20°C	0.53% by wt.
Solubility of water in solvent at 20°C	1.27% by wt.
Specific gravity at 20/20°C	0.8162
Refractive index at 20°C	1.4068
Specific heat at 25°C	0.553 cal./g
Surface tension at 25°C	25.2 dynes/sq cm
Vapor pressure at 20°C	5.2 mm Hg
Viscosity at 20°C	0.0074 poise
Weight per gallon at 20°C	6.79 lbs.

Methyl Hexyl Ketone (Octanone-2) [$CH_3(CH_2)_5CO \cdot CH_3$]. A colorless liquid with a characteristic odor, methyl hexyl ketone is used as a solvent for vinyl compounds and dyes, and has been found particularly suitable in dispersing dyes in light petroleum oils for newsprint inks.

Purity	95%, min.
Specific gravity at 20°C	0.81–0.83
Weight per gallon at 20°C	6–8 lbs.

Diisobutyl Ketone (Valerone) [$(C_4H_9)_2CO$]. A water-white, stable liquid, miscible with most organic liquids, diisobutyl ketone has good solvency for cellulose acetate, nitrocellulose, vinyl resins, waxes, gums, natural and synthetic resins, and crude rubber. It is used principally as a high-boiler in nitrocellulose lacquers and vinyl resin coatings, where its slow evaporation rate is advantageous. It may be used in chemical synthesis where it may be condensed with amines and other groups to give compounds that will react with its carbonyl group. The resulting substances may be used in dyes, rubber accelerators, inhibitors, insecticides and pharmaceuticals.

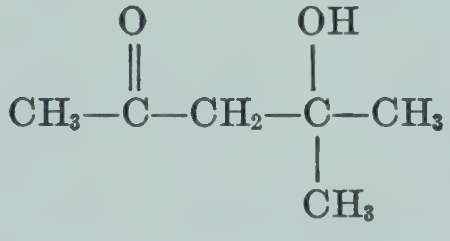
Typical Properties and Specifications

Boiling point	168.1°C
Dilution ratio (xylene)	1.5
Flash point	140°F
Specific gravity at 20/20°C	0.9407
Solubility in water at 20°C	0.06% by wt.
Solubility of water in solvent at 20°C	0.45% by wt.
Vapor pressure at 20°C	1.7 mm Hg
Weight per gallon at 20°C	6.8 lbs.
Acidity (as acetic)	0.05% by wt. (max.)
Boiling range at 760 mm	95% between 165°–175°C

Water	Miscible with 19 vol. 60° Bé gasoline at 20°C

Diisobutyl ketone is an excellent dispersant for the preparation of organosols containing little or no plasticizer. In the past it has been difficult to prepare these dispersions when they contain less than 15 per cent plasticizer. However, using diisobutyl ketone, it is now possible to formulate semi-hard or hard metal coatings using the organosol technique. These unplasticized organosols may also be blended with plastisols for thinning to coating viscosity and to raise the resin-to-plasticizer ratio. Diisobutyl ketone is also an efficient dispersant in plasticized organosols, producing stable, low viscosities. It is a good solvent for "Vinylite" resin VYNV at temperatures used in fusing organosols, but exerts little solvent action at room temperature. This insures good knitting of the hot resin particles and results in higher tensile and tear strength in the film. In nitrocellulose lacquers, it controls the evaporation rate and improves blush resistance.

Diacetone Alcohol (Diacetone, 4-hydroxy-4-methylpentanone-2, pyranton A, diacetonyl alcohol)



$$CH_3-\overset{\overset{O}{\|}}{C}-CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{OH}{|}}{C}}-CH_3$$

Diacetone alcohol is a flammable liquid that is colorless when pure, becoming yellow on ageing; it has a mint-like odor. Made by the condensation of acetone, the commercial product contains up to 15% of acetone. For this reason the technical product is superior in its solvent power to the acetone-free grade. It is miscible with most organic liquids, as well as with water. It is a good solvent for cellulose acetate, nitrocellulose, cellulose acetobutyrate, cellulose acetopropionate, hydrocarbons, oils, fats, resins, gums and dyes. It has only limited solvency for dammar gum, polyvinyl acetate and the petroleum resins. A high-boiling solvent, diacetone alcohol also exhibits the desirable properties of reducing the viscosities of organic solutions of high solids content, and of minimizing temperature effects on viscosities. In most respects it is quite similar to acetone with the exception of a very much slower rate of evaporation.

It is used in cellulose ester lacquers, particularly of the brushing type, where it produces brilliant gloss and hard film and where its lack of odor is desirable. It is used in lacquer thinners, dopes, wood stains, wood preservatives and printing pastes; in coating compositions for paper and textiles; in making artificial silk and leather; in imitation gold leaf; in celluloid cements; as a preservative for animal tissue; in metal-cleaning compounds;

in the manufacture of photographic film; and in hydraulic brake fluids, where it is usually mixed with an equal volume of castor oil.

Diacetone alcohol is available in two grades: technical, containing up to 15% acetone, and acetone-free.

Typical Properties and Specifications (acetone-free grade)

Boiling point at 760 mm	167.9°C
Coefficient of expansion (Cubical)	0.000533 per °F
Color	Water-white to light straw
Flash point (open cup)	144°F
Heat of combustion	8,601 cal./g
Melting point	−47°C
Specific gravity at 20/20°C	0.937 to .946
Refractive index at 20°C	1.4235
Viscosity (Saybolt)	
113 seconds at	−12°C
674 seconds at	−30
1980 seconds at	−48
Weight per gallon at 20°C	7.83 lbs.
Acidity (as acetic)	0.05%
Distillation range at 760 mm	
Below 135°C	None
Below 158	Not more than 5%
Above 170	None
Non-volatile matter	0.005% by wt. (max.)

Acetonyl Acetone (Hexanedione-2,3) $[(CH_3\cdot CO\cdot CH_2)_2]$. Acetonyl acetone, a diketone, is a water-white liquid with an agreeable odor. It is completely soluble in water, almost entirely soluble in such substances as toluene, kauri gum and rosin, and only partly soluble in raw linseed oil, shellac, dewaxed dammar and ester gum. It has been suggested as an intermediate in the manufacture of rubber accelerators, dyes, inhibitors, insecticides, and pharmaceuticals and for the preparation of derivatives of thiophene, furan and pyrrole. It may also be employed in tanning hides and skins.

Typical Properties and Specifications

Boiling point	191.4°C
Dilution ratio (xylene)	1.8
Flash point	158°F
Specific gravity at 20/20°C	0.9710–0.9760
Solubility in water at 20°C	Complete
Vapor pressure at 20°C	0.5 mm Hg
Weight per gallon at 20°C	8.10 lbs.
Acidity (as acetic)	0.020% by wt., max.
Boiling range at 760 mm	185 to 195°C
Purity	98.0% by wt., min.
Water	Miscible with 19 vol. 60° Bé gasoline at 20°C

Mesityl Oxide (4-Methyl-3-pentenone-2, isopropylidone acetone, methyl isobutenyl ketone) $[(CH_3)_2C{:}CH \cdot CO \cdot CH_3]$. Mesityl oxide is an unsaturated, medium-boiling ketone made by the dehydration of diacetone alcohol. It is a colorless to straw-yellow, oily liquid with a peppermint-like odor. It will darken and form a solid residue on exposure and ageing. It is miscible with most organic liquids and it is a good solvent for such substances as nitrocellulose, ethylcellulose, low-viscosity cellulose acetate, polyvinyl chloride, vinyl resins, hydrocarbons, raw linseed oil, kauri gum, rosin, ester gum and synthetic rubber. It will only partly dissolve shellac and dewaxed dammar.

Mesityl oxide is used in lacquers and thinners where its presence in the solution lowers the viscosity and gives it both a high tolerance for hydrocarbons and resistance to humidity. Its excellent solvent power for gums and resins is especially applicable in vinyl-type resins, where it produces films that are tough, glossy and have good flow; its presence permits use of larger proportions of aromatic hydrocarbon diluents.

Typical Properties and Specifications

Boiling point at 760 mm	129.5°C
Coefficient of expansion	0.000599 per °F
Color	Straw-yellow
Dielectric constant at 20°C	15.4
Flash point (Tag closed cup)	83°F
Heat of combustion	846.7 Cal. per mol
Heat of vaporization	85.9 cal./g
Melting point	−59°C
Solubility in water at 25°C	3.4% by vol.
Solubility of water in solvent at 20°C	3.4% by wt.
Specific gravity at 20/20°C	0.853–0.856
Specific heat (21–121°C)	0.521 cal./g
Refractive index at 20°C	1.4456
Vapor pressure at 20°C	8.0 mm Hg
30	14.3
40	24.5
Viscosity at 25°C	8.79 millipoises
Weight per gallon at 20°C	7.12 lbs.
Acidity (as acetic)	0.05%, max.
Distillation range (ASTM)	Below 120°C None Above 135 None More than 95% distills over Below 131°C
Purity	95% by wt., min.
Water	Miscible without turbidity with 19 vols. of 60° Bé gasoline at 20°C (approx. 0.20% by wt.)

Cyclic Ketones

Cyclohexanone (Sextone, anon, pimelin ketone, keto hexamethylene) $(\underline{\mathrm{CO\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2}})$. Cyclohexanone is a colorless to pale yellow, stable liquid with an odor suggestive of peppermint. It is made by the dehydrogenation of cyclohexanol. It is miscible in all proportions with most solvents, especially the common lacquer solvents and diluents, hydrogenated and chlorinated hydrocarbons, phenols, pyridine, and turpentine. It is a good solvent for cellulose ethers, esters, basic dyes, latex, fats, blown oils, waxes, crude rubber, and such gums and resins as ester gum, alkyds, vinyls, coumarone, 100% and modified phenol resins, cyclohexanone resins and many natural resins. It forms constant-boiling mixtures with camphor, tetrachloroethane, and trichloropropane. It has a very high dilution ratio as compared with the coal-tar hydrocarbons, a fact which accounts for its excellence as a solvent, especially in the lacquer industry.

Its low rate of evaporation and strong solvent powers impart blush resistance, good flow and working qualities to lacquers and give films that are clear, smooth and glossy and show good adhesion. It is also used in spraying and brushing lacquers and as a medium boiler. It is particularly effective for blending nitrocellulose with spirit-soluble and hydrocarbon-soluble resins and oils. Its solvency for basic dyes makes it applicable in wood stains. Other uses are in the air-drying and stoving type of synthetic resins, in plastics and molding powders, in paint and varnish removers, in spot and stain removers, in metal-degreasing preparations, in polishes, printing inks, as a leveling agent in dyeing, in delustering cellulose acetate, insecticides, and pharmaceuticals.

Typical Properties and Specifications

Boiling point	155.6°C
Color	Water-white to pale yellow
Dielectric constant at 25°C	18.2
Evaporation rate, approximate (toluene = 100)	20
Flash point (open cup)	130°F
Freezing point	−45°C
Solubility in water at 20°C	8.7%
Specific gravity at 20°C	0.944–0.950
Specific heat 15–18°C	0.433 cal./g
Refractive index	1.443–1.451
Viscosity (S.U.V. at 100°F)	33
Weight per gallon at 20°C	7.9 lbs.
Acidity	Neutral
Distillation range	95% within 151–157°C
Purity	98–100%
Residue	0.02%
Water content	0.2% max.

TABLE 13.13.—KETONE SOLVENT PROPERTIES AFFECTING BLUSH RESISTANCE[4]

SOLVENT	SOLUBILITY OF:		WET-BULB DEPRESSION (°C)
	Solvent in H_2O	H_2O in solvent	
Acetone	Infinite	Infinite	30.5
Methyl ethyl ketone	22.6	9.9	21.5
Methyl propyl ketone	6.0	3.6	12.0
Methyl butyl ketone	3.44	3.70	6.5
Methyl amyl ketone	1.95	2.15	3.0
Ethyl acetate	7.9	3.0[a]	21.5
n-Butyl acetate	2.3	2.4	6.5

[a] For C.P. product containing no alcohol; commercial material dissolves more water than this.

TABLE 13.14.—BLUSHING TESTS ON LACQUERS CONTAINING KETONES, ETC.[4]

Standard Formula	Solvent % by volume
14 grams (wet) ½-sec. R. S. nitrocellulose	60 toluene
5 grams Ester gum	10 *n*-butyl alcohol
5 grams dibutyl phthalate	20 ethyl acetate
100 cc. solvent	10 other solvent

DRY BULB		WET BULB		DIFFERENCE (°F)	RELATIVE HUMIDITY %	BEHAVIOR OF LACQUER WHEN OTHER SOLVENT IS:				
(°F)	(°C)	(°F)	(°C)			Me Pr ketone	Me Bu ketone	Me Am ketone	*n*-Butyl acetate	*sec*-Butyl acetate
87	30.6	85	29.4	2	92	−	−	−	−	−
87	30.6	84	28.9	3	89	−	−	−	−	−
86	30	83	28.3	3	89	−	−	−	−	−
82	27.8	79	26.1	3	88	−	−	±	−	−
87	30.6	83	28.3	4	85	−	−	±	±	−
86	30	82	27.8	4	85	−	±	+	±	−
85	29.4	81	27.2	4	85	−	±	+	±	−
83	28.3	79	26.1	4	85	−	±	+	±	−
87	30.6	82	27.8	5	81	−	±	+	±	−
85	29.4	80	26.7	5	81	±	+	+	+	±
84	28.9	79	26.1	5	80	±	+	+	+	+
87	30.6	81	27.2	6	77	+	+	+	+	+
85	29.4	79	26.1	6	77	±	+	+	+	+
87	30.6	79	26.1	8	70	+	+	+	+	+

− Bad blush; ± slight blush; + no blush.

Methyl Cyclohexanone (Methyl anon, sextone B) [meta: $CO \cdot CH_2 \cdot CH(CH_3) \cdot CH_2 \cdot CH_2 \cdot CH_2$; para: $CO \cdot CH_2 \cdot CH_2 \cdot CH(CH_3) \cdot CH_2 \cdot CH_2$]. Methyl cyclohexanone is a water-white to pale yellow liquid with an acetone-like odor. It is a mixture of two isomeric cyclic ketones made by the dehydrogenation of methyl cyclohexanol. It closely resembles cyclohexanone in its physical properties, miscibility, tolerance for non-solvents and solvent action. It differs from cyclohexanone in its somewhat slower evaporation rate and lower dilution ratios with aromatic hydrocarbons. Methyl cyclohexanone is especially suitable for phenolic and alkyd resins, crude rubber, nitrocellulose, ester gum and kauri. It is also an excellent agent for blending pyroxylin with resins, oils and rubber in lacquers. It is used in crystallizing lacquers, where its low evaporation rate retards evaporation sufficiently to permit crystal growth. It is also used in slow-setting varnish removers and in rubber cements.

Typical Properties and Specifications

Boiling point	169.0–170.5°C
Evaporation rate (approximate) (toluene = 100)	20
Flash point	53°C
Freezing point	−70°C
Refractive index at 25°C	1.442–1.446
Solubility in water at 20°C	2–3%
Specific gravity at 25/4°C	0.910–0.914
Viscosity (S.U.V. at 100°F)	33
Weight per gallon	7.6 lbs.
Distillation range	165.0–172°C 95% distills within 3.0°
Purity	98–100%
Residue	None
Water content	0.2%, max.

Isophorone (3,5,5-Trimethylcyclohexene-2-one-1)

$$[\underline{CO\cdot C(CH_3):CH\cdot CH_2\cdot CH_2\cdot C}(CH_3)_2].$$

Isophorone is a stable, colorless, volatile liquid with a mild odor. It is only slightly soluble in water but miscible with most lacquer solvents. It is an excellent solvent for many types of cellulose esters, cellulose ethers, oils, fats, gums and resins, both natural and synthetic. It is the most pow-

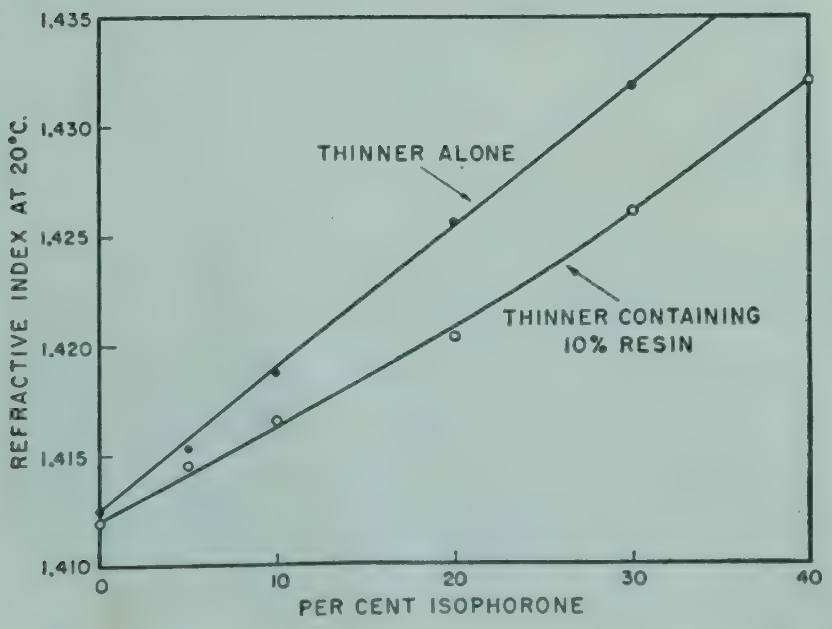


FIGURE 13.23. Absorption of Isophorone-Troluoil Thinners by Resin VYNW.

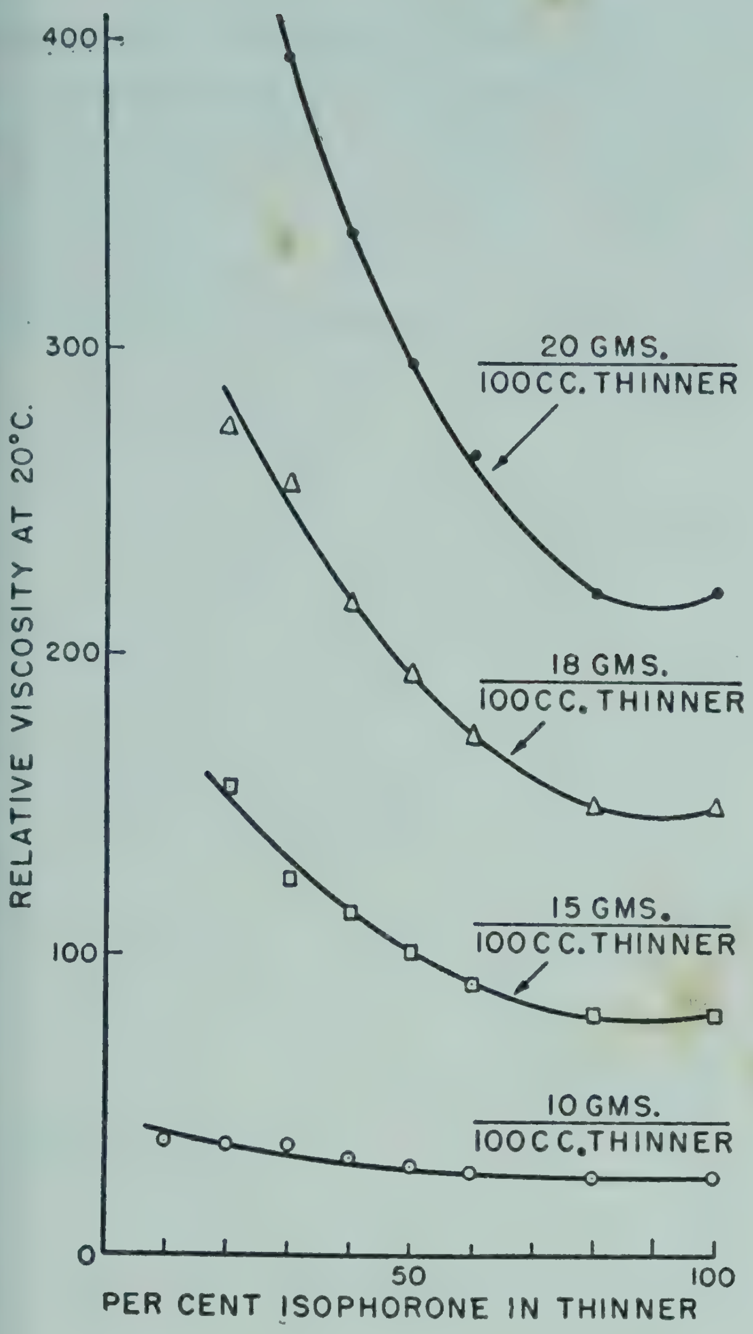


FIGURE 13.24. Relative Viscosities of Resin VYHH in Isophorone-Xylene Mixtures.

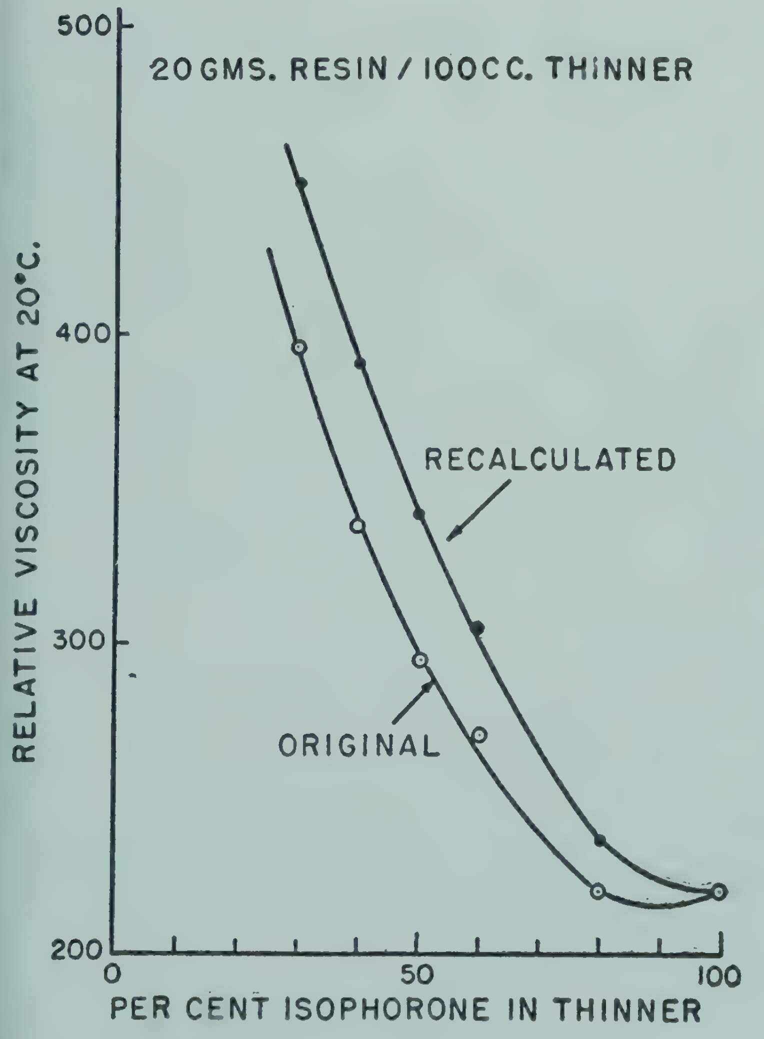


FIGURE 13.25. Equilibrium Viscosity of R Resin VYHH in Isophorone-Xylene Mixtures at 20 Grams per 100 Cc. Thinner.

erful solvent for nitrocellulose and "Vinylite" resins. Isophorone has one of the highest aromatic hydrocarbon dilution ratios for nitrocellulose—5.7 for toluene and 5.1 for xylene. It will dissolve 30% of "Vinylite" resin without gelling. At ordinary temperatures solutions can be made of $\frac{1}{2}$-second R. S. nitrocellulose containing 45 per cent solids. Isophorone is used in the manufacture of coatings, inks, stencil pastes and as a thinner in synthetic resin finishes.

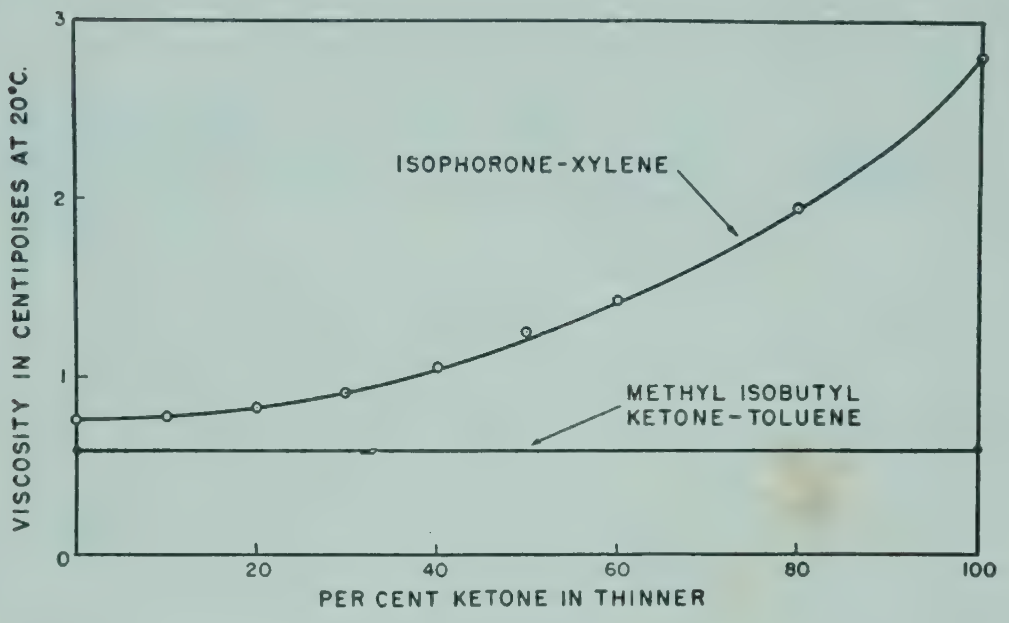


Figure 13.26. Viscosity of Solvent Mixtures.

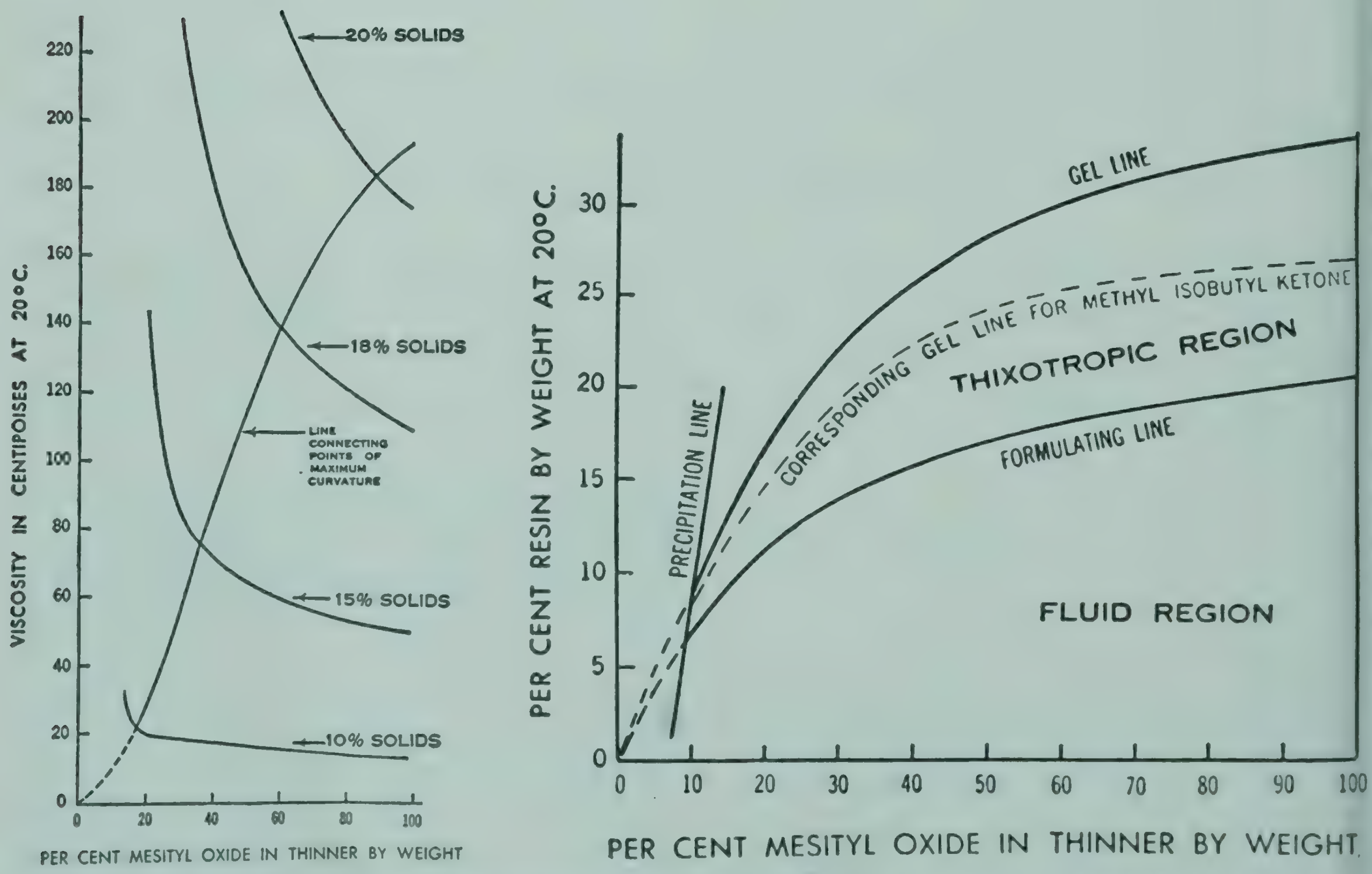


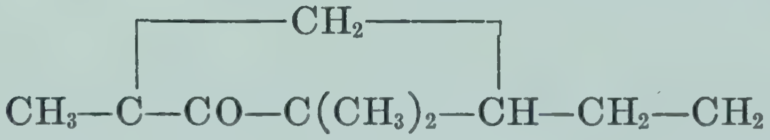
Figure 13.27. Equilibrium Viscosities and Phase Diagram of Resin VYHH in Mesityl Oxide-Toluene Mixtures.

Typical Properties and Specifications

Boiling point at 760 mm	215.2°C
Dilution ratios	
Toluene	5.7
Xylene	5.1
Troluoil	1.0
Mineral spirits	0.7
Flash point (open cup)	205°F
Freezing point	−8.1°C
Solubility in water at 20°C	1.2% by wt.
Solubility of water in solvent at 20°C	3.8% by wt.
Specific gravity at 20/20°C	0.9200–0.9250
Vapor pressure at 20°C	0.25 mm hg
Weight per gallon at 20°C	7.68 lbs.
Acidity (as acetic)	0.02% by wt., max.
Distillation range at 760 mm	205 to 220°C
Color	Not darker than 0.05 g $K_2Cr_2O_7$ per liter of water
Purity	98.0% by wt., min.
Water content	Miscible with 19 vol. 60° Bé gasoline at 20°C

TERPENE KETONES

Fenchone



$$CH_3{-}\overbrace{C{-}CO{-}C(CH_3)_2{-}CH}^{CH_2}{-}CH_2{-}CH_2$$

Fenchone is a liquid ketone closely resembling camphor.

Boiling point	191.0°	
Dilution ratio:		
with coal-tar naphtha	1.3 Final conc. 8.0	
with hi-flash naphtha	1.2 Final conc. 8.2	
Kauri-Butanol	All proportions Kauri-Butanol in 50% sol. with mineral spirits 131	
Optical activity	+7.4	
Refractive index at 20°C	1.4625	
Specific gravity at 15.5°C	0.9457	
Aniline point (—)	54°C (Calculated from 50:50 min. spts.)	
Distillation range	5%	193.0°C
	10%	193.4
	20%	193.8
	40%	194.2
	60%	194.5
	80%	195.4
	90%	196.0
	95%	197.5

"Hercosol No. 80" is a mixture of terpene ketones such as fenchone and camphor and dipentene. It is a high-boiling solvent having a solvent action almost equal to pine oil and its uses are therefore similar to those of pine oil.

Color (Lovibond 500 Amber Series Glasses)	3.0
Flash point	145°F
Kauri-Butanol solvency value	Infinite
Refractive index at 20°C	1.4732
Specific gravity at 15.5/15.5°C	0.880
Aniline point	Below −20°C
Boiling range (ASTM)	
5%	181.0°C
30%	184.6
70%	189.0
95%	209.5
Water content	0.05%

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Chapter 14

Acids

The fatty acids are so called because they are found naturally in animal fats. Their original source has also suggested the names by which they are known, such as formic acid from red ants (formicae), butyric acid from butter (butyrum), caproic acid from goats (caper). In recent years, however, these and many others have been produced commercially by synthetic processes. Generally, the lower acids have a pronounced odor and are freely soluble in water, but as they rise in the series, they acquire the characteristics of hydrocarbons, with a corresponding decrease in their acidity, water-solubility and specific gravity. These acids are interesting chiefly because of their derivatives, which are formed by the replacement of the hydrogen atom in the carboxyl group by metals or alkyl radicals. Thus salts or esters are formed as well as such other derivatives, known as halides, anhydrides, peroxides, and amides. All these are useful in lacquers, plasticizers, varnish driers, synthetic flavors, antiseptics, and pharmaceuticals.

The cellulose esters of the higher acids impart excellent weather resistance to surface coatings. Anhydrides, derivatives of organic acids, are superior to their corresponding acids in forming esters, and are therefore used where the acid would otherwise be too weak. They are also used for reactions with the hydroxyl groups found in such substances as sugars, phenols and cellulose. Anhydrides are used as catalysts in nitrations, sulfonations and other reactions, where water is split off.

Lewis, Brauns and Buchanan[1] prepared a number of lignin esters of mono and dibasic aliphatic acids and determined their solubility in a number of solvents.

Acetic Acid (Vinegar acid, methane carboxylic acid, ethanoic acid) (Ch_3COOH). Acetic acid is a colorless liquid with a pungent odor; it is made synthetically from acetylene or by the oxidation of alcohol. It is soluble in water, alcohols, ethyl ether, and other organic solvents. It is used as a precipitant for albumen, casein, and rubber latex. It is also employed in the manufacture of leather, cordage, linoleum, acetate solvents, acetyl derivatives, dyes, matches, printing inks, and polishes, and as an assistant in dyeing processes.

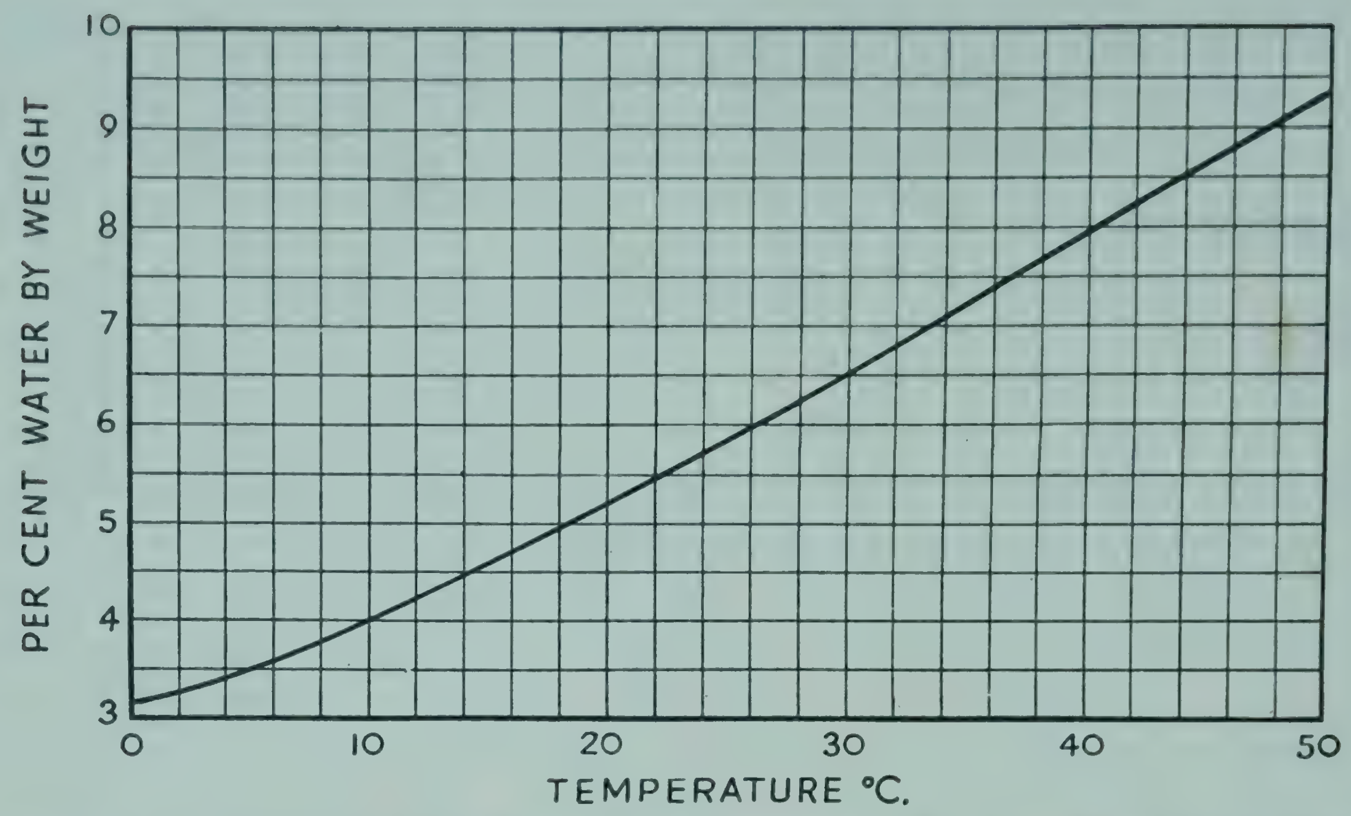


FIGURE 14.1. Solubility of Water in Caproic Acid at Various Temperatures.[2]

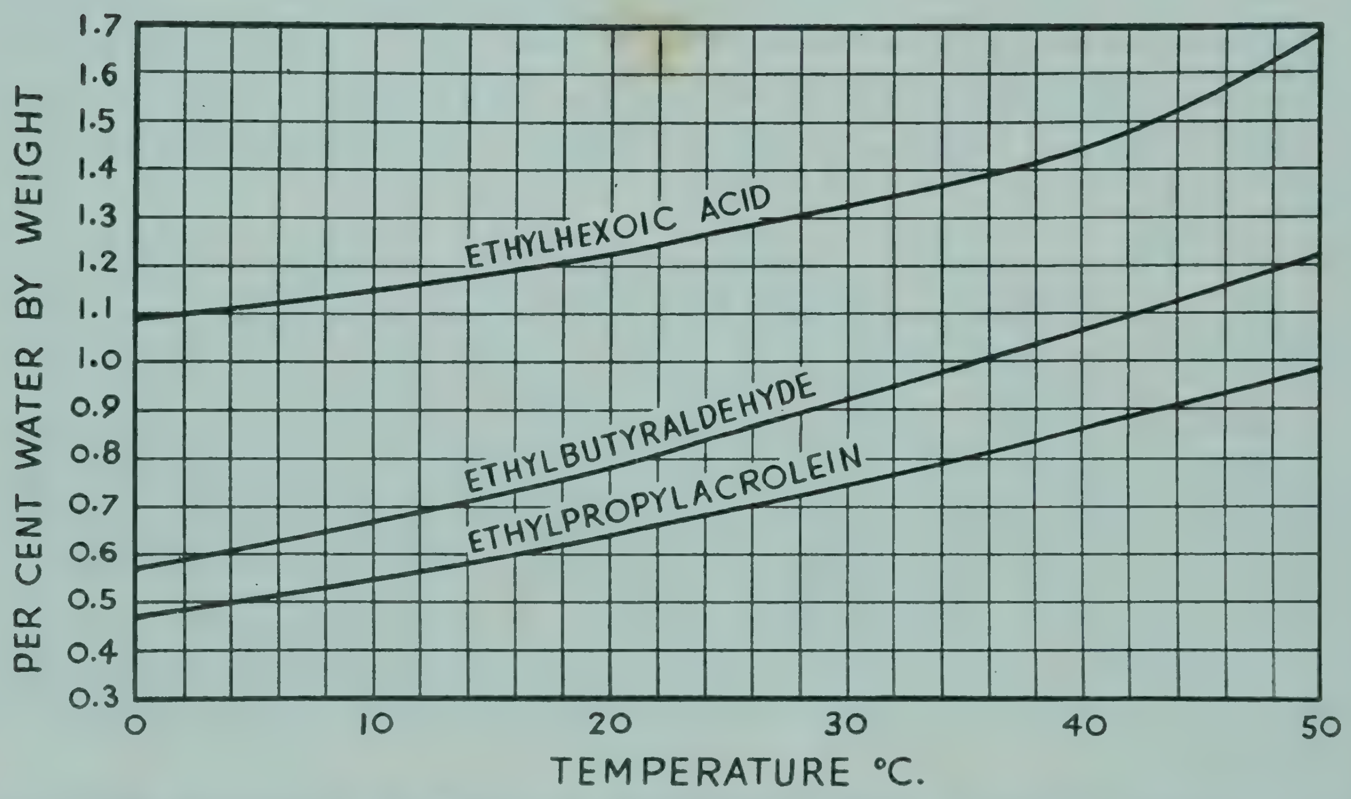


FIGURE 14.2. Solubility of Water in Ethylhexoic Acid at Various Temperatures.[2]

Physical Properties

Dissociation constant	1.86×10^{-5} recip. ohm
Boiling point	118.1°C
Freezing point	16.7°C
Specific gravity at 20/4°C	1.049

Specifications (Glacial Acetic)

	Standard + Laundry Special	U.S.P. XII	C.P.
Acetaldehyde	0.05% (max.)		
Acidity, as acetic acid	99.5% (min.)	99.5% (min.)	99.8% (min.)
Color	Water-white	Water-white	Water-white
Formic acid	0.2% (max.)	—	0.00% (max.)
Freezing point	15.6°C (min.)	15.6°C (min.)	16.24°C (min.)
Non-volatile matter	—	0.0265% (max.)	0.0008% (max.)
Water content	0.5% (max.)	0.5% (max.)	0.2% (max.)
Weight per gallon at 20°C	8.74 lbs.	8.74 lbs.	8.74 lbs.

Butyric Acid (Ethylacetic acid, butanoic acid, propylformic acid) ($CH_3CH_2CH_2COOH$). Butyric acid is a water-white liquid having a characteristically pronounced and highly disagreeable odor. It is soluble in most organic solvents and completely soluble in water. The importance of butyric acid is found in its butyrate, made with alcohols; these compounds are used as flavors because of their pleasant fruity odors. Other uses are in the manufacture of flavor esters, plastics, drugs, in leather tanning and for deliming hides.

Typical Properties and Specifications

Boiling point at 760 mm	163.5°C
Coefficient of expansion at 20°C	0.001026°C
at 55	0.001064
Color	Water-white
Critical temperature	355°C
Critical density	0.302
Dissociation constant at 25°C	1.48×10^{-5} recip. ohm
Electrical conductivity at 25°C	0.00039×10^{-4} recip. ohm
Flash point (ASTM open cup)	170°F
Heat of combustion	5905 cal. (15)/g
Heat of fusion	20.1 cal. (15)/g
Heat of vaporization	1.59 cal./g
Melting point	−5.7°C
Solubility in water at 20°C	Complete
Solubility of water in solvent at 20°C	Complete
Specific gravity at 20/20°C	0.9595
Specific heat	0.514 (20–100°C)
Refractive index at 19°C	1.3980
Surface tension at 20°C	26.8 dynes/sq cm
Vâpor pressure at 20°C	0.84 mm Hg
Viscosity at 25°C	0.01529 poise
Weight per gallon at 20°C	7.985 lbs.
Chlorides	None
Distillation range at 760 mm	160–165°C
Purity	99.0% by wt., min.

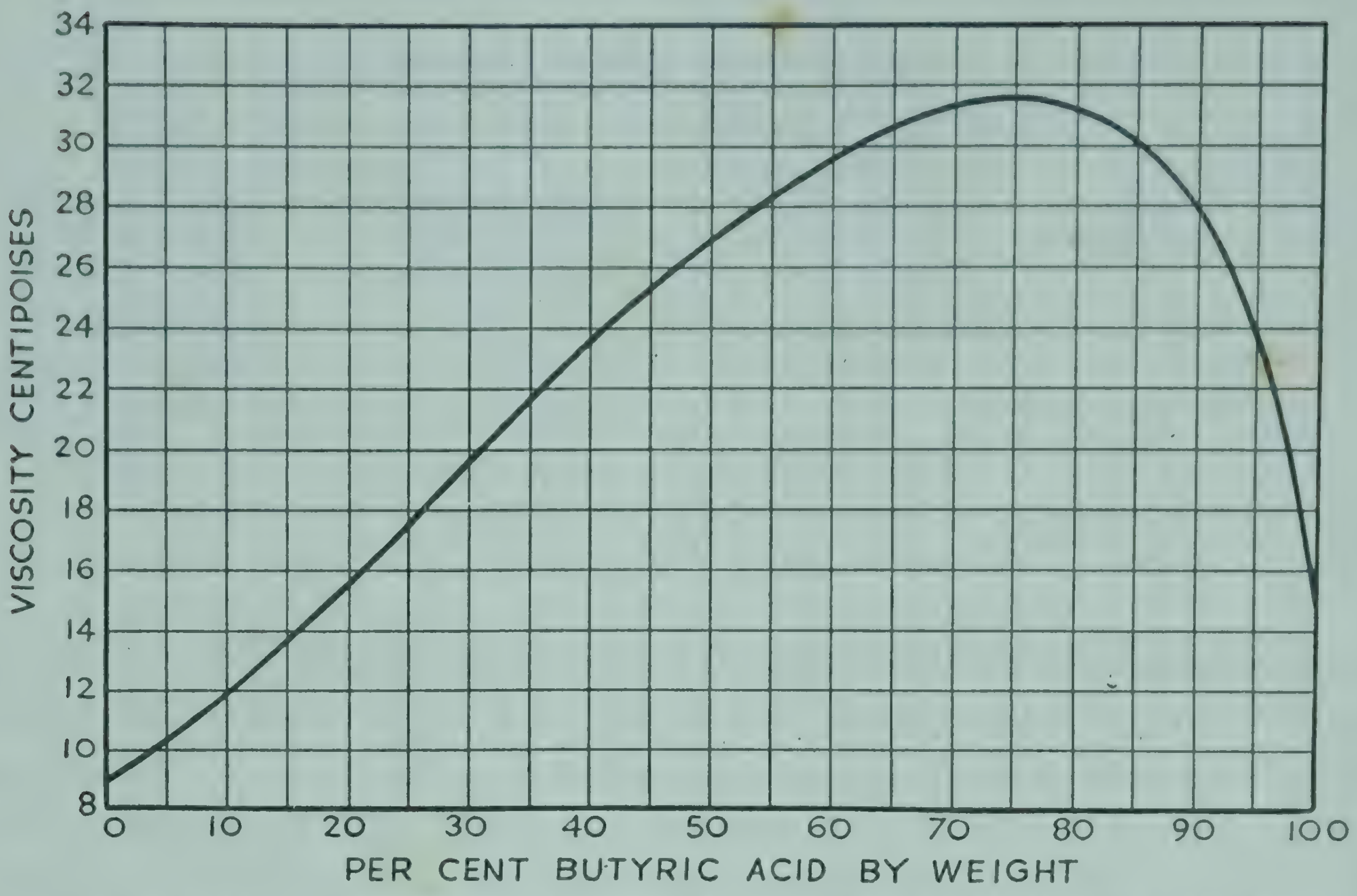


FIGURE 14.3. Viscosity of Aqueous Butyric Acid Solution at 25°C.[2]

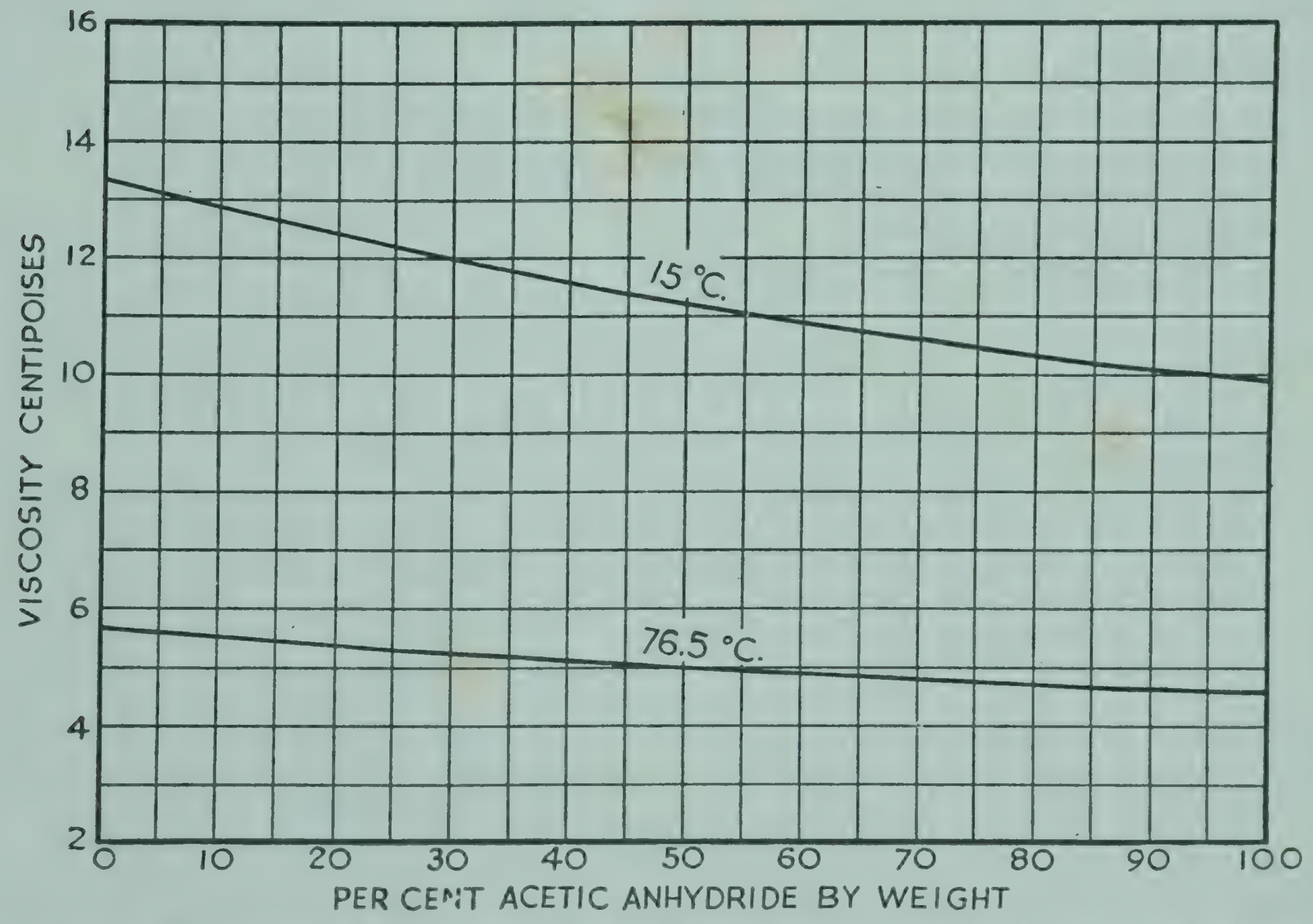


FIGURE 14.4. Viscosity of Acetic Acid and Acetic Anhydride Mixtures at 15°C and 76.5°C.

Butyric Anhydride [$(C_3H_7CO)_2O$]. Butyric anhydride is a water-white liquid which hydrolyzes to butyric acid in the presence of water. Like butyric acid, it is used in making butyrates, flavors, drugs and tanning agents.

Boiling point at 760 mm	199.5°C
Color	Water-white

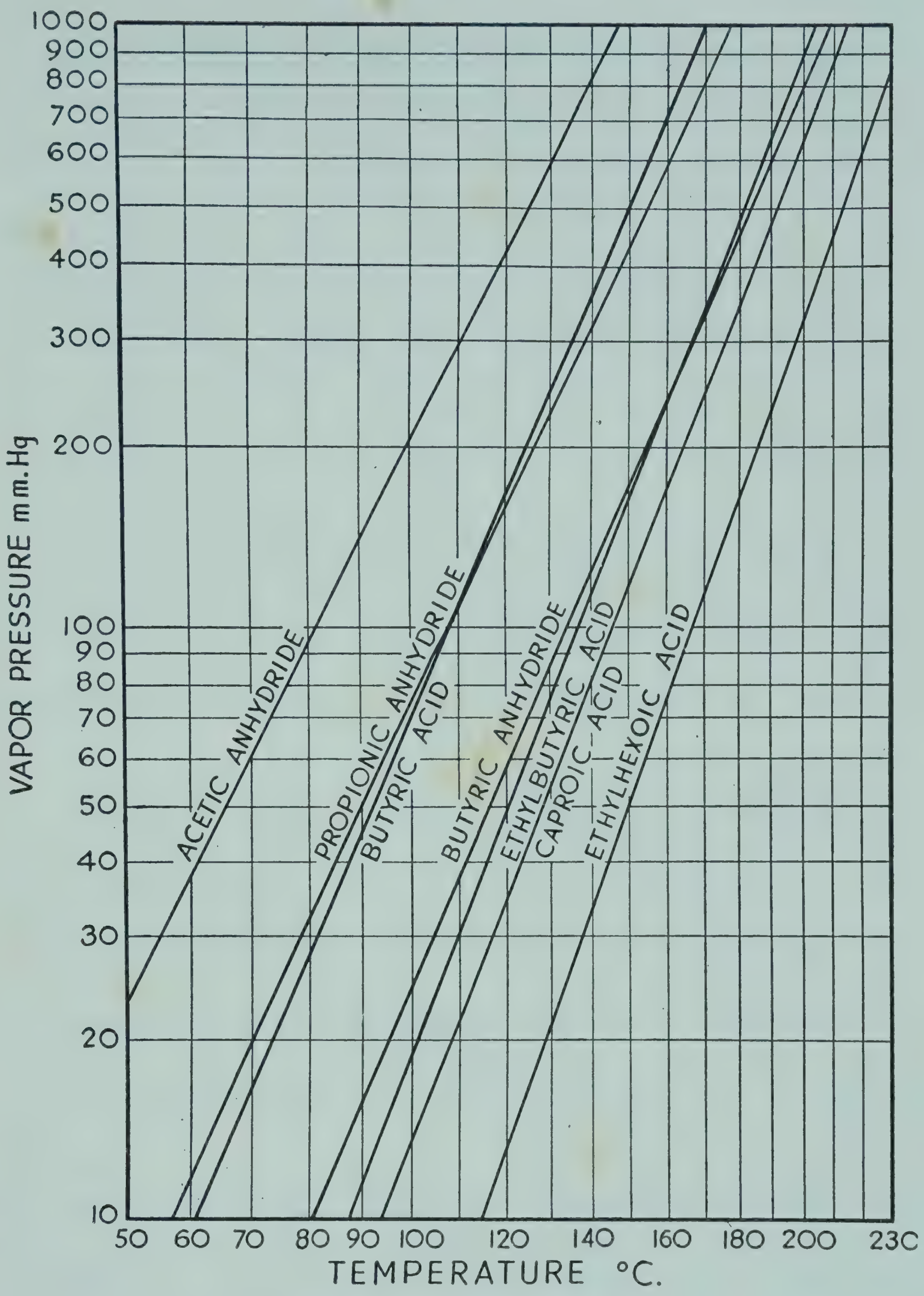


FIGURE 14.5. Vapor Pressures.[2]

Flash point	190°F
Melting point	−75°C
Specific gravity at 20/20°C	0.965–0.970
Vapor pressure at 20°C	0.37 mm Hg
Weight per gallon at 20°C	8.1 lbs.
Distillation range at 760 mm	None
Below 190°C	
Above 200	None
Below 195	Not more than 10%
Purity	85% by wt., min.

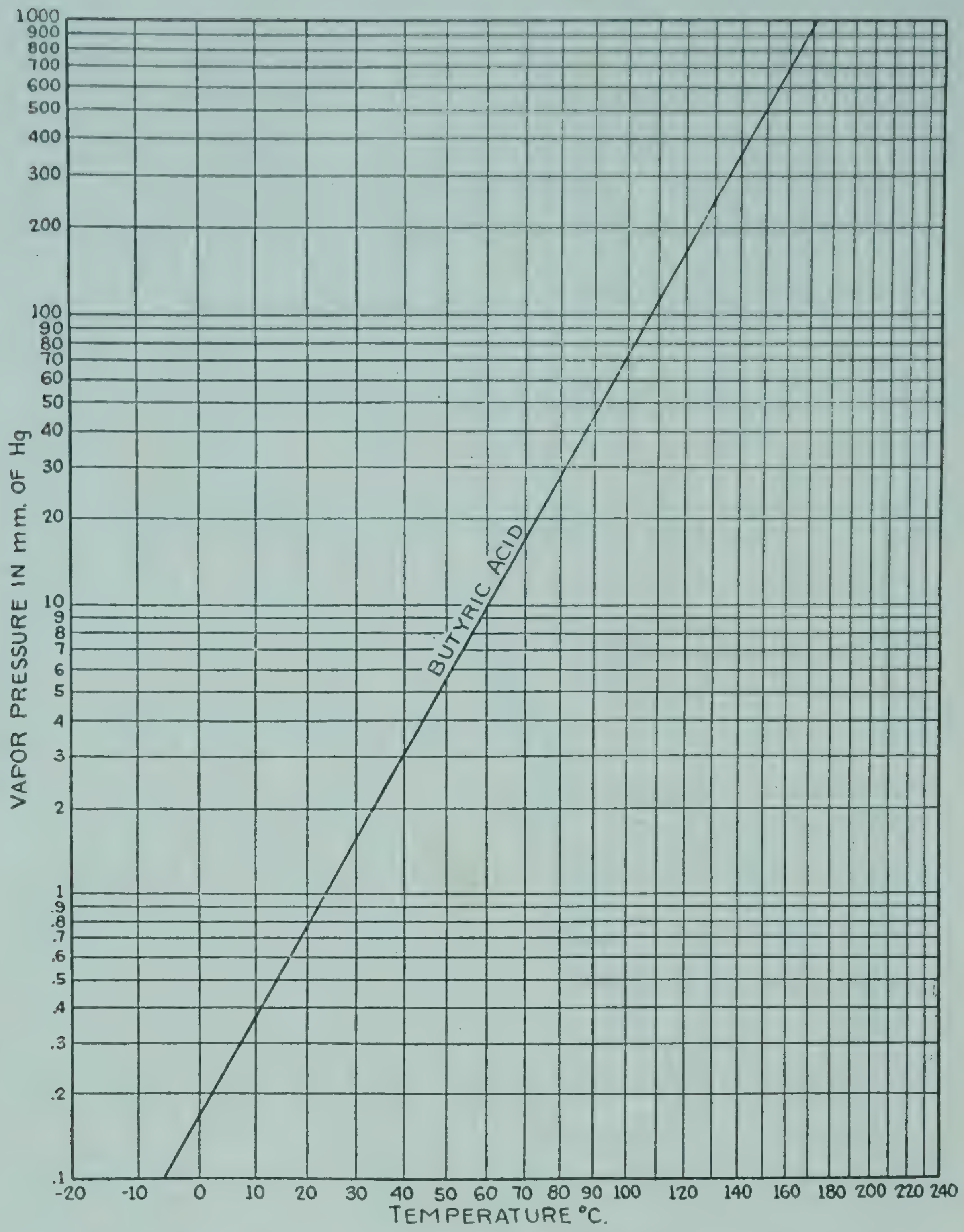


FIGURE 14.6. Vapor Pressure of Butyric Acid at Various Temperatures.[2]

Lactic Acid (alpha-Hydroxypropionic acid) ($CH_3CHOH \cdot CO_2H$). Lactic acid, which is among the oldest of the known organic acids, is obtained from sour milk by the reduction of hexose sugars or by the interaction of acetaldehyde and carbon monoxide. It is miscible with water and many organic reagents. Since it has an asymmetrical carbon atom, lactic acid exists in two optical isomeric forms. Peckham[3] states that "the nomenclature used to designate the isomeric forms was, until recently, very confusing. The form of the acid commonly known as sarcolactic, the form occurring in blood, has (+) rotation but the *l* configuration. It is therefore correctly designated as *l*(+) lactic acid and its mirror image as *d*(−) lactic acid. The salts of the *l*(+) form are levorotatory and the salts of the *d*(−) form are dextrorotatory. Because of the low optical rotatory power of the

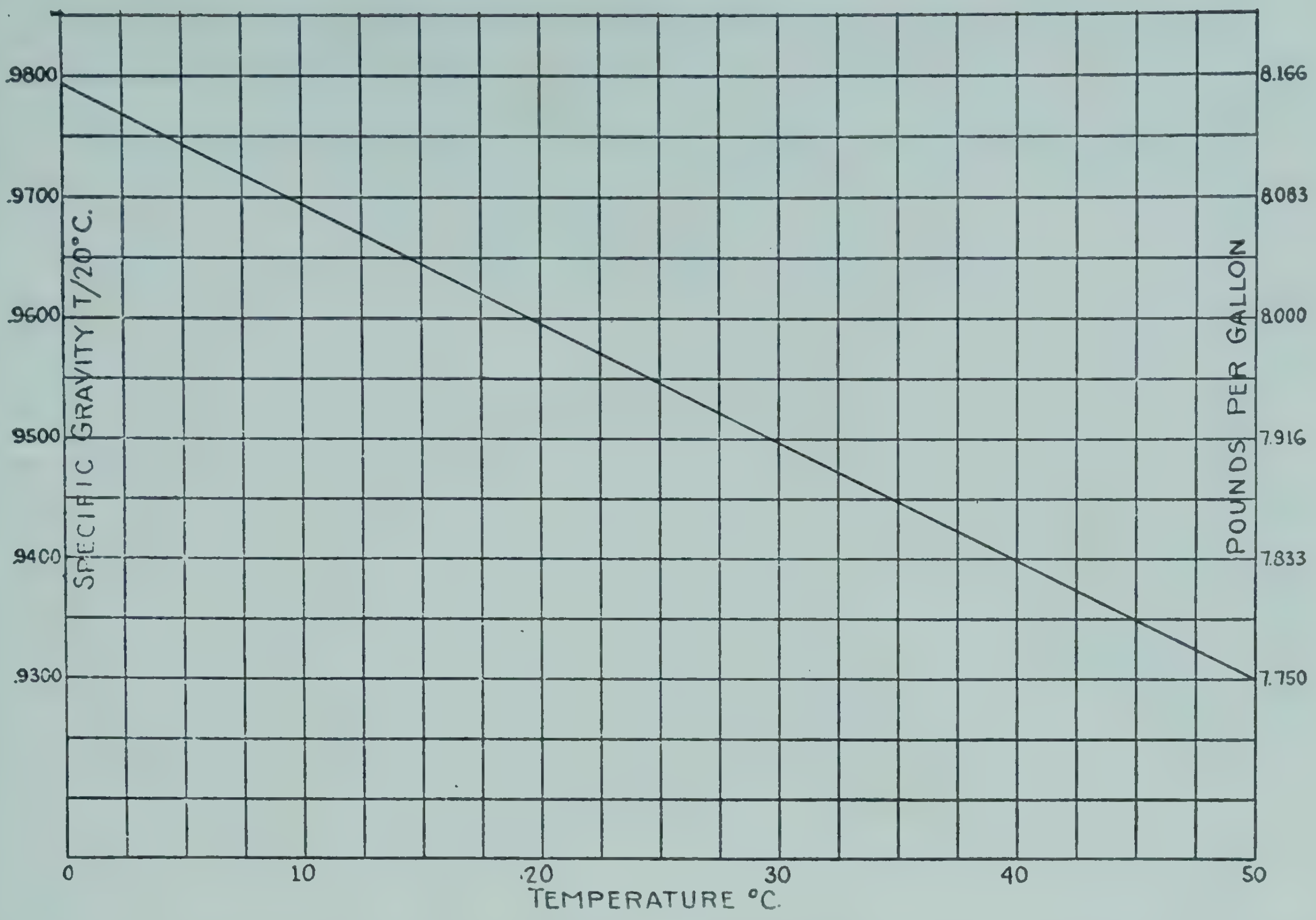


FIGURE 14.7. Specific Gravity and Weight per Gallon of Butyric Acid at Various Temperatures.[2]

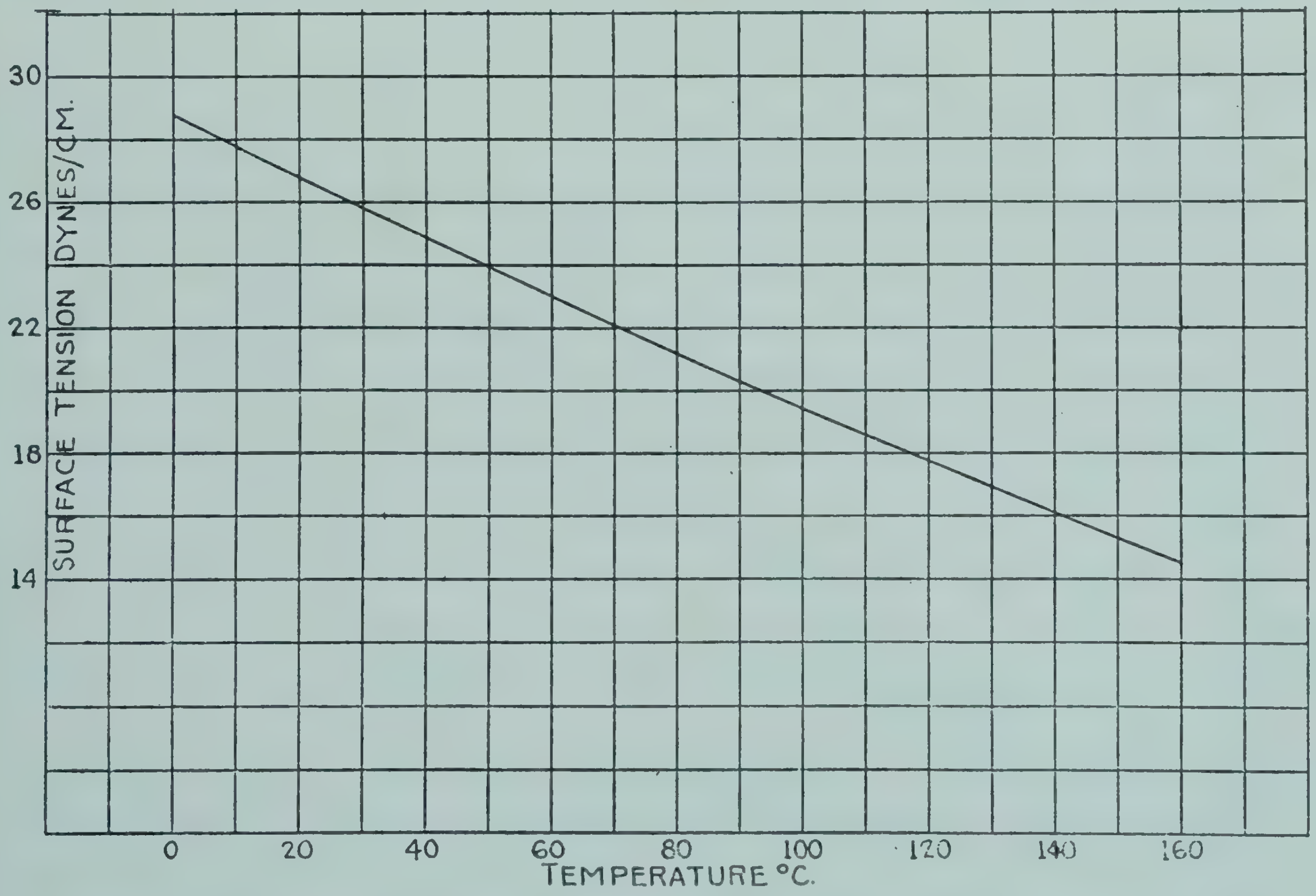


FIGURE 14.8. Surface Tension of Butyric Acid at Various Temperatures.[2]

free acids, rotation of the pure acid or its simple salts is not a suitable criterion for establishing the optical form of the acids, or the percentage composition in case of a mixture."

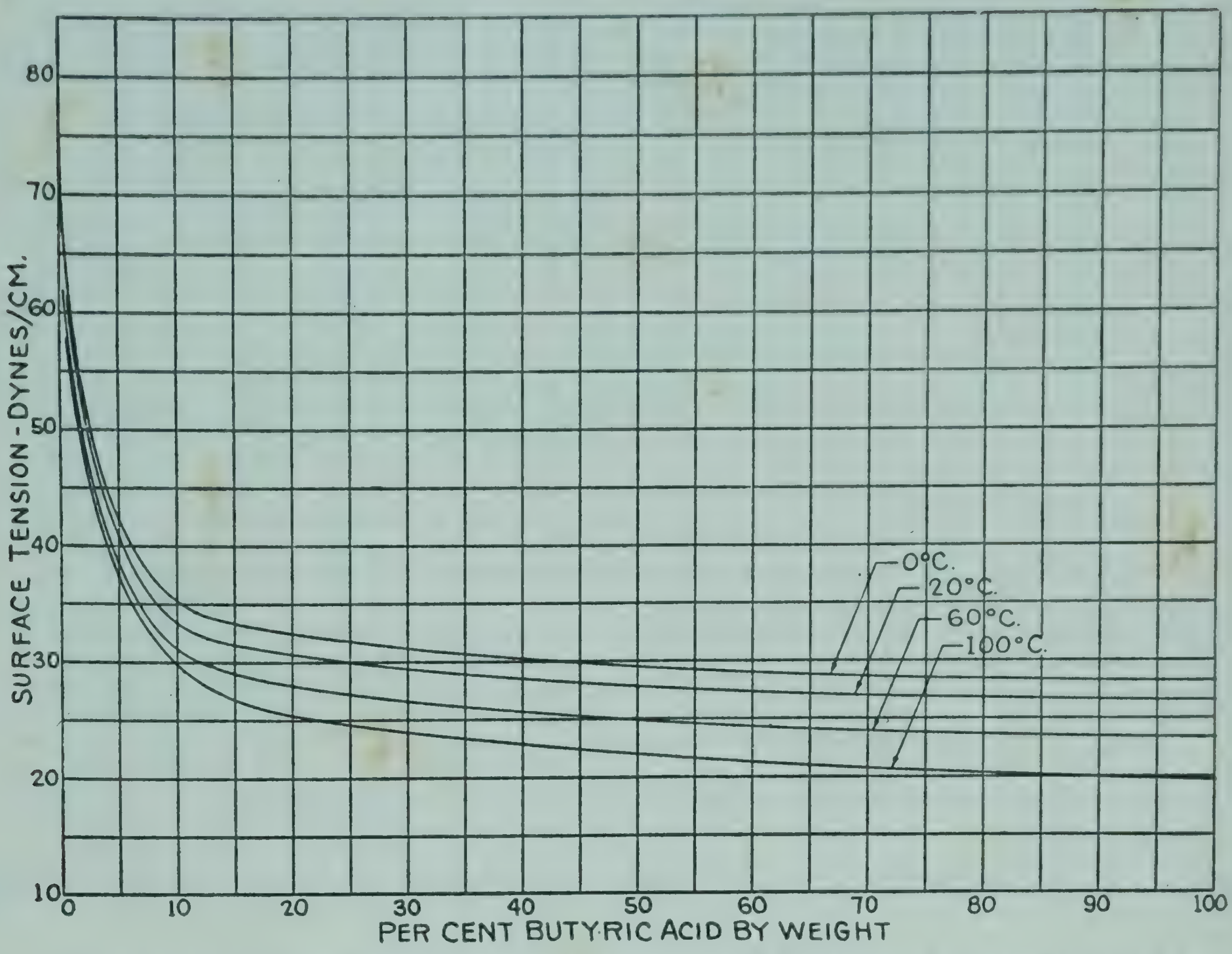


FIGURE 14.9. Surface Tension of Aqueous Solutions of Butyric Acid.[2]

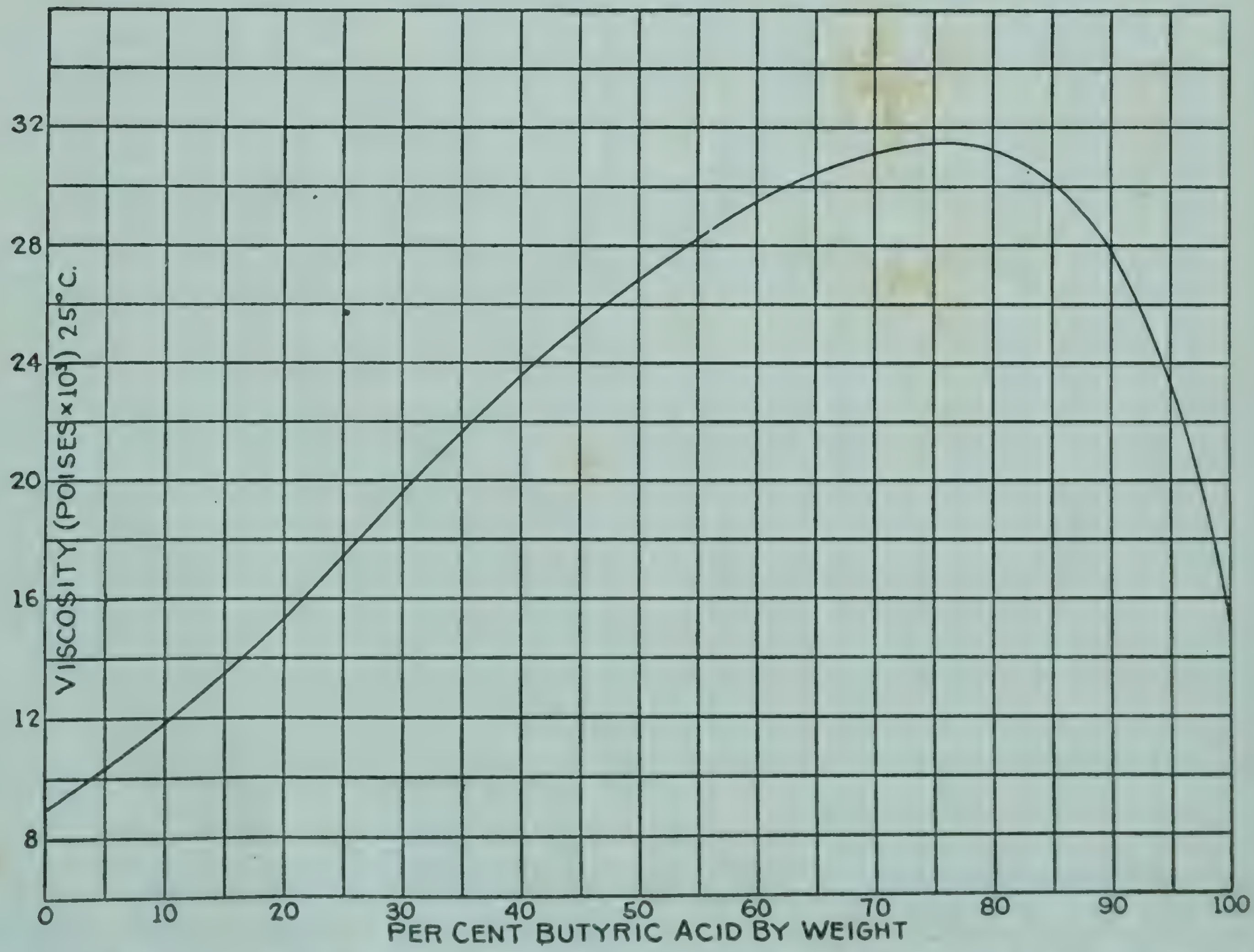


FIGURE 14.10. Viscosity of Aqueous Solutions of Butyric Acid at 25°C.[2]

TABLE 14.1.—SOLUBILITIES[a] OF ESTERS OF HARDWOOD ALKALI LIGNIN

ACYL GROUP	METHANOL	ETHANOL	ACETONE	CHLOROFORM	ETHER	DIOXANE	BENZENE	PETROLEUM ETHER	ETHYL ACETATE
Monobasic Acid Esters									
Acetyl	1	1	3	3	0	3	2	0	3
Propionyl	1	1	3	3	0	3	2	0	3
Butyryl	1	1	3	3	1	3	3	0	3
Isobutyryl	1	1	3	3	1	3	3	0	3
Valeryl	1	1	3	3	1	3	3	0	3
Isovaleryl	1	1	3	3	1	3	2	0	3
Caproyl	0	0	3	3	2	3	2	0	3
Isocaproyl	1	1	3	3	2	3	3	0	3
Heptoyl	0	0–1	3	3	2–3	3	3	0	3
Decanoyl	0–1	0			2–3			0–1	
Undecanoyl	0	0	3	3	2	2–3	2–3	0–1	3
Lauroyl	0	0	3		2–3	3	3	1	3
Tridecanoyl	0	0	3		2	2–3	2–3	2–3	
Myristoyl	0–1	0–1	3	3	3	3	3	2–3	3
Palmitoyl	1	1			3	3	3		3
Stearoyl	0–1	0–1	3		3	3	3	3	3
Oleoyl			3		3	3	3	2–3	
Aliphatic Dibasic Acid Esters									
Succinyl			2	1	0	2	0		
Adipyl I	0–1	0	0–1		0	0–1	0	0	
Adipyl II	0–1	0	2–3		0	2–3	0		
Suberyl	0–1	0–1	1	0	0	2	0	0	
Azelayl	1	0–1	2	0–1	0	2	0	0	0–1
Aromatic Acid Esters									
Phthalyl I	0	0	1–2	0–1	0	1–2	0	0	0
Phthalyl II	0	0	1–2	0	0	1–2	0	0	0
Benzoyl	0	0	2	3	0	3	2	0	1
p-Toluene-sulfonyl	0	0	1	2	0	3	0	0	0

[a] 0 = insoluble; 1 = below 10%; 2 = 10–50%; 3 = above 50% (very soluble).

Commercial lactic acid has been determined[4] to be a mixture of alpha-hydroxypropionic acid, lactyllactic acid, and water. When dilute lactic acid is concentrated, two molecules of lactic acid unite to form lactyllactic acid and water. The lactyllactic acid splits off from the water thus:

$$\begin{array}{l} 2CH_3CHOH\cdot COOH \rightleftarrows CH_3\cdot CHOH\cdot COOCH(CH_3)\cdot COOH + H_2O^{4,5} \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad \downarrow\uparrow \\ \qquad\qquad\qquad\qquad\qquad\quad \underbrace{CH(CH_3)OCOCH(CH_3)OCO} \end{array}$$

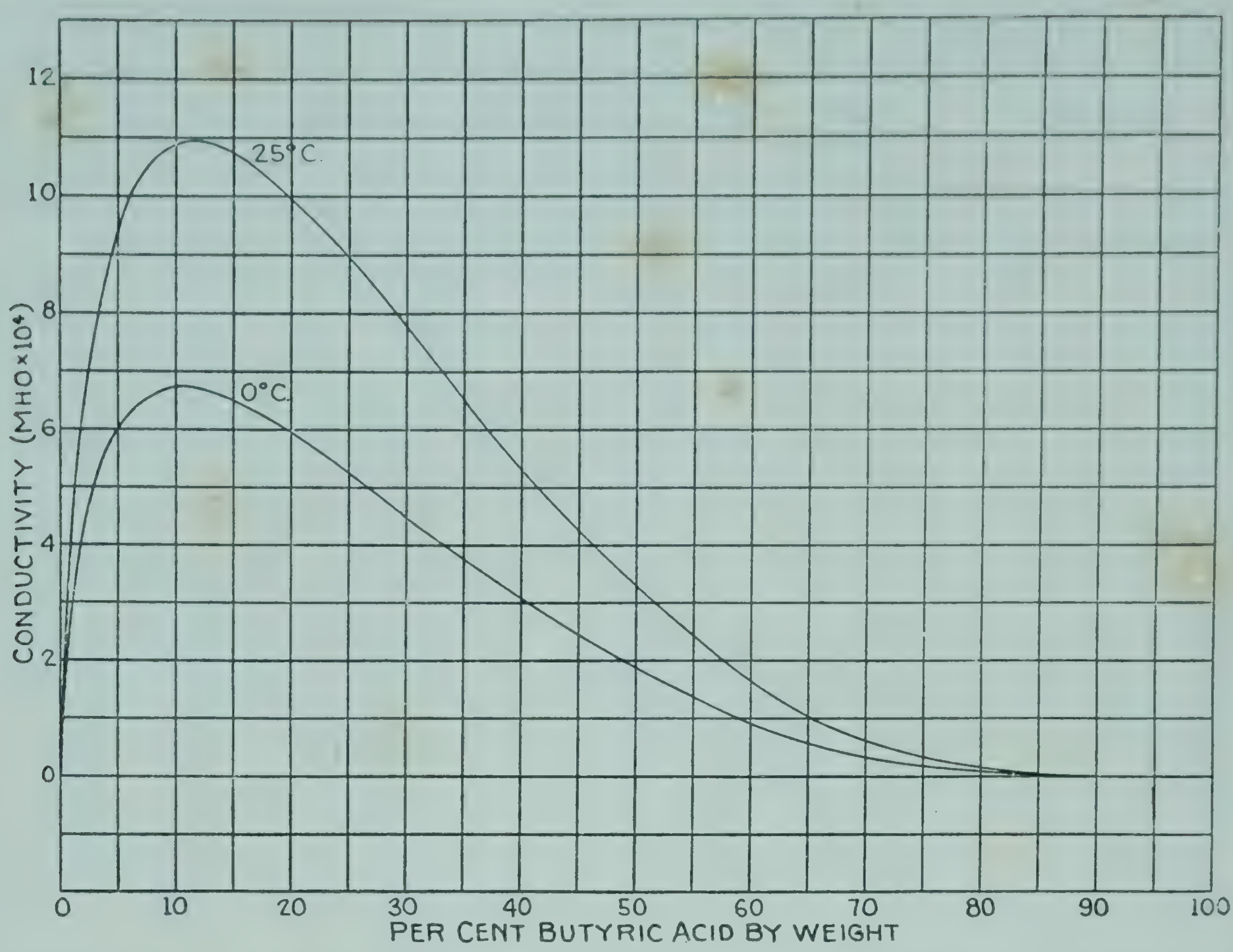


Figure 14.11. Electrical Conductivity of Aqueous Solutions of Butyric Acid.[2]

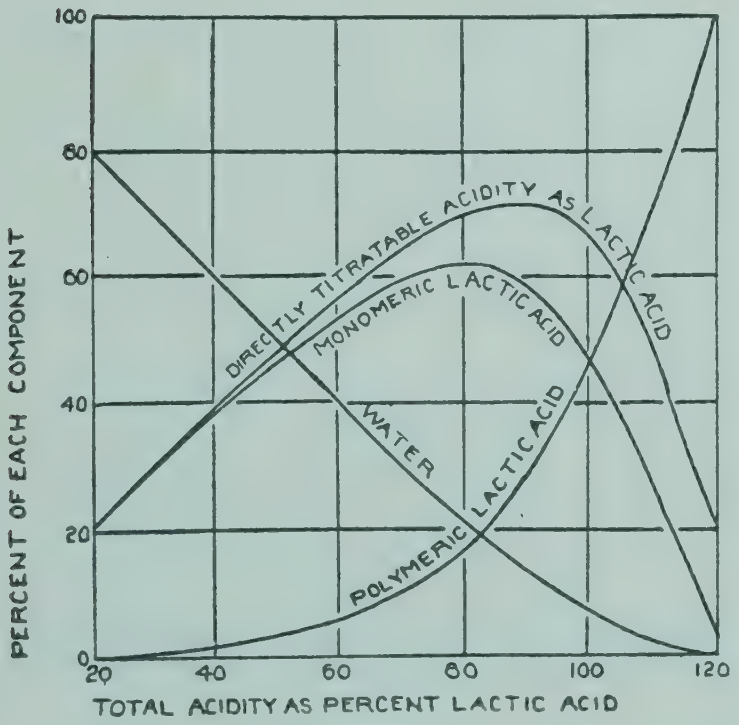
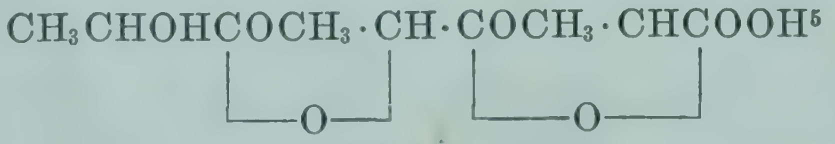


Figure 14.12. A graph showing the Composition of Aqueous Lactic Acid Systems at Equilibrium and at Progress States of Dehydration.[3]

Polylactyllactic acids may also be formed by loss of water between the carboxyl and the alcohol groups, thus:



$$CH_3CHOH\underbrace{COCH_3\cdot CH}_{O}\cdot\underbrace{COCH_3\cdot CH}_{O}COOH^{5}$$

dilactyllactic acid

The conditions which affect the production of a lactic acid solution from lactyllactic acid are temperature, concentration and age of solution. This can be observed in the fact that when at room temperature, lactyllactic acid is converted to lactic acid only after several weeks, but the process is greatly hastened with heat.

Boiling point at 14 mm	122°C
Melting point	18°C
Specific gravity at 15/4°C	1.249

2-Ethylbutyric Acid (Diethyl acetic acid, 2-ethylbutanoic acid) [$(C_2H_5)_2CHCOOH$]. 2-Ethylbutyric acid is a water-white liquid, similar to butyric acid in most of its properties, except that its odor is less strong and it is not as soluble in water. Its halogenated derivatives are finding use in the manufacture of drugs. Its esters with higher glycols are outstanding vinyl resin plasticizers.

Boiling point at 760 mm	194°C
Flash point	210°F
Solubility in water at 20°C	0.22% by wt.
Solubility of water in solvent at 20°C	3.3% by wt.
Specific gravity at 20/20°C	0.9225
Vapor pressure at 20°C	0.14 mm Hg
Weight per gallon at 20°C	7.68 lbs.
Distillation range at 760 mm	185–200°C
Purity	90% by wt., min.

2-Ethylhexoic Acid (Octoic acid, 2-Ethylhexanoic acid) [$CH_3(CH_2)_3CH(C_2H_5)COOH$]. This acid possesses a mild odor and a high boiling point. It is important for its metallic esters, the properties of which suggest usefulness as varnish driers. These metallic salts are stable, mild-odored, light-colored compounds, and are soluble in hydrocarbons. The glycol esters of this acid are excellent vinyl resin plasticizers.

Boiling point at 760 mm	226.9°C
Flash point	260°F
Solubility in water at 20°C	0.25% by wt.
Solubility of water in solvent at 20°C	1.2% by wt.
Specific gravity at 20/20°C	0.9077
Vapor pressure at 20°C	0.03 mm Hg
Weight per gallon at 20°C	7.55 lbs.
Distillation range at 760 mm	220 to 230°C (90% distills within this range)
Purity	95% by wt. min.

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3. Peckham, G. T., *Chem. Eng. News*, **22:** 440 (1944).
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Chapter 15

Ethers

Ethers have the type formula R—O—R, indicating that they are made up of two hydrocarbon groups held together by an oxygen atom. They are made from two molecules of the corresponding alcohol by removal of one molecule of water. Compared with alcohols, ethers are characterized by their greater volatility, by lower solubility in water, and by higher solvent power for oils, fats and greases. Because of their stability and ease of recovery ethers are widely used for extraction purposes. Mixtures of the lower alkyl ethers with alcohols make efficient solvents for cellulose esters. The so-called epoxides (cyclic ethers) differ from other ethers, which are chemically inert, by being highly active chemically because of their unstable three-membered rings. Since the epoxides react with the labile hydrogen atom of water, alcohols, amines, and similar substances, they form a wide range of industrially important compounds.

The glycol ethers, which have developed into important tonnage chemicals during the last twenty years, contain both ether and alcohol groups in their molecules and have the solvent characteristics of both. Principal members of this family are the ethers of ethylene glycol, or "Cellosolve" solvents, and ethers of diethylene glycol, or "Carbitol" solvents. These stable, odorless compounds are excellent solvents for nitrocellulose and find wide use in the manufacture of lacquers and thinners. They also possess high dilution ratios for coal-tar and petroleum diluents and permit the addition of a considerable amount of solids without increasing the viscosity of the solutions. These compounds are used as solvents for dyestuffs, and wood stains, as brake fluid diluents, as mutual solvents in cutting oils, soluble oils, insecticides, dry-cleaning soaps, and leather compounds where the immiscible liquids are blended, and in the manufacture of commercially important plasticizers. Recently the "Propylsolve" solvents, or ethers of propylene glycol have become available in tankcar quantities.

ALKYL ETHERS

Ethyl Ether (Ether, ethyl oxide, sulfuric ether) (C_2H_5—O—C_2H_5). Ethyl ether is a colorless, highly flammable and very volatile liquid with a sweetish, pleasant odor. Its vapors are heavier than air and are strongly narcotic. It was first made in 1840 from ethyl alcohol and sulfuric acid, a method

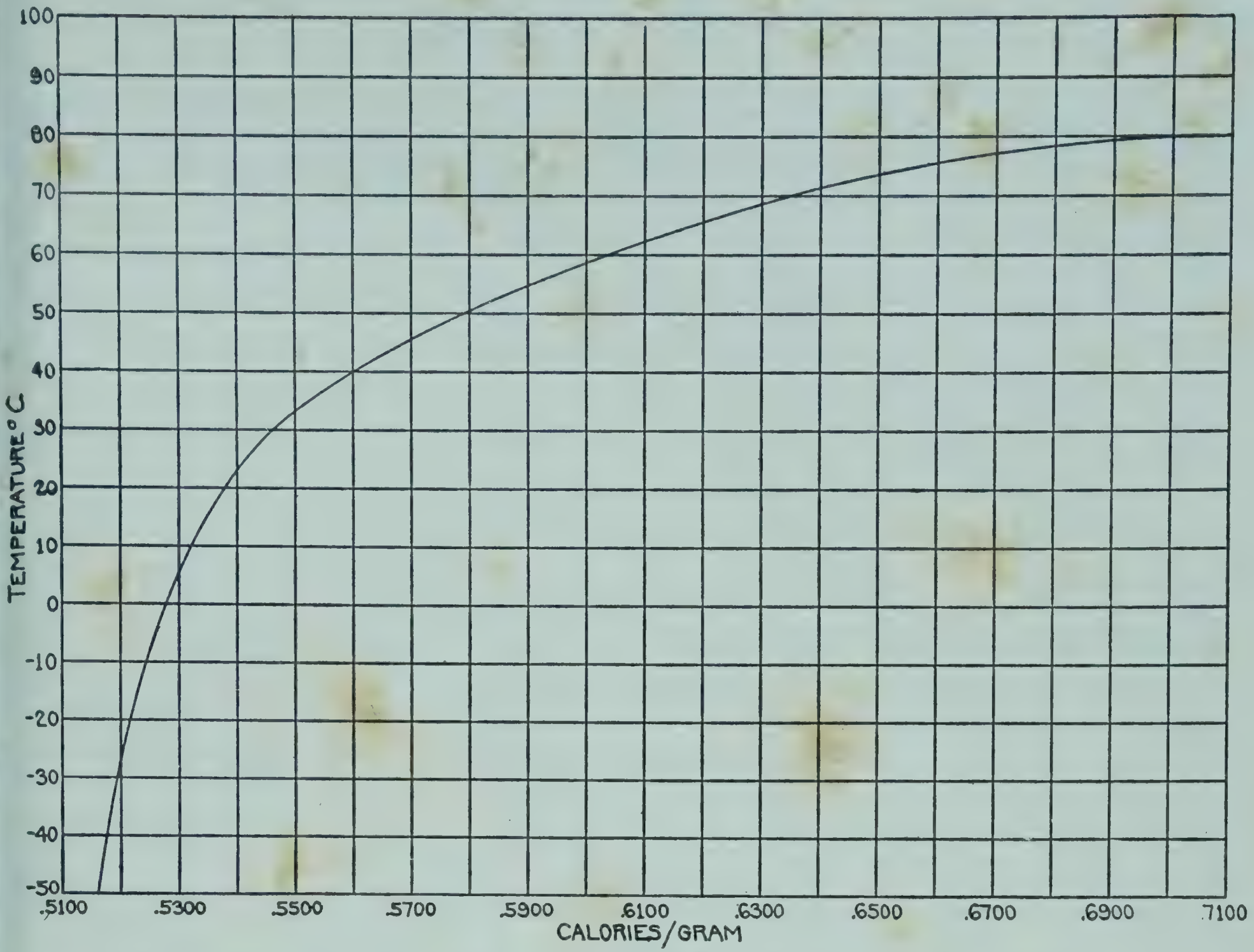


FIGURE 15.1. Specific Heat of Ethyl Ether at Various Temperatures.[1]

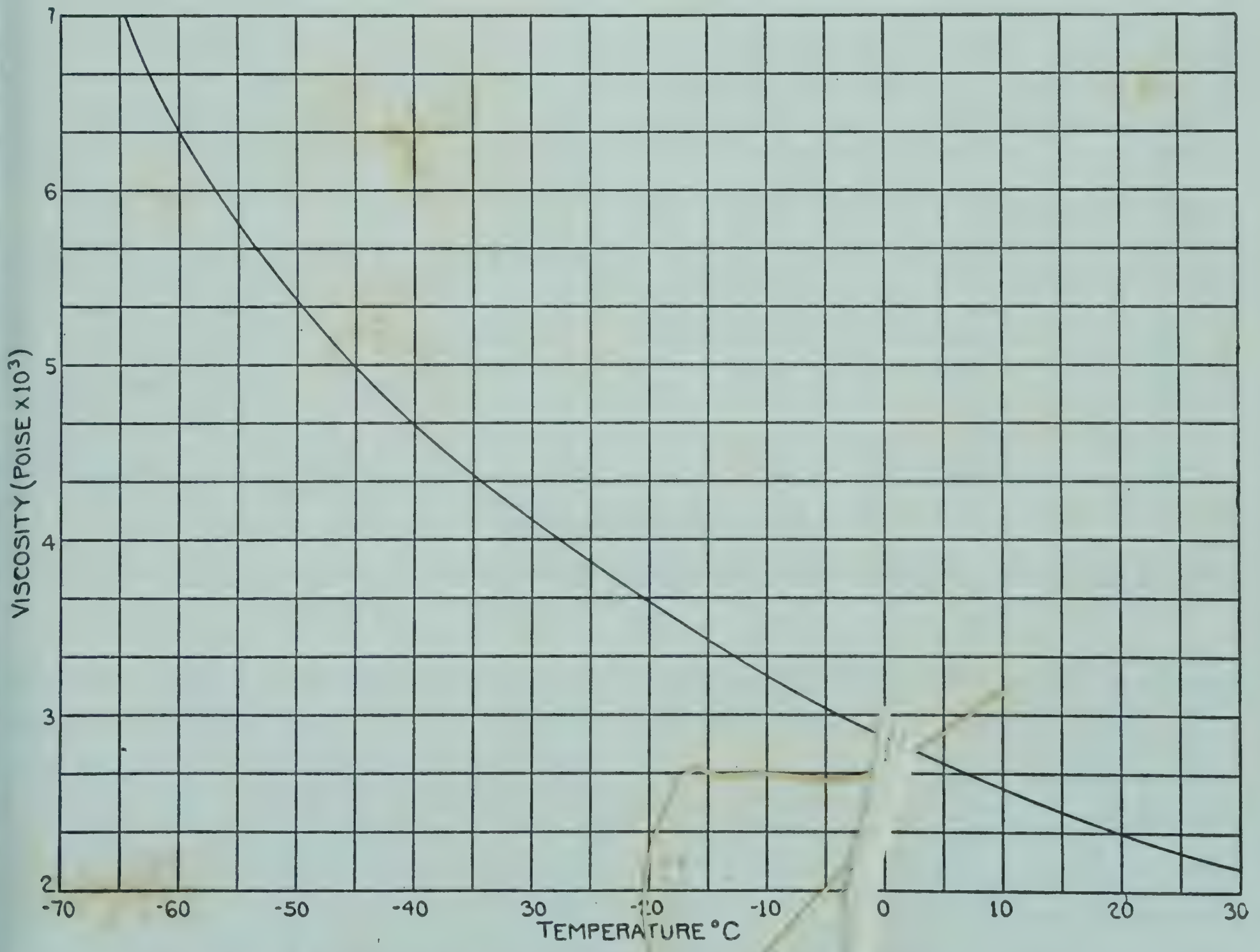


FIGURE 15.2. Viscosity of Ethyl Ether at Various Temperatures.[1]

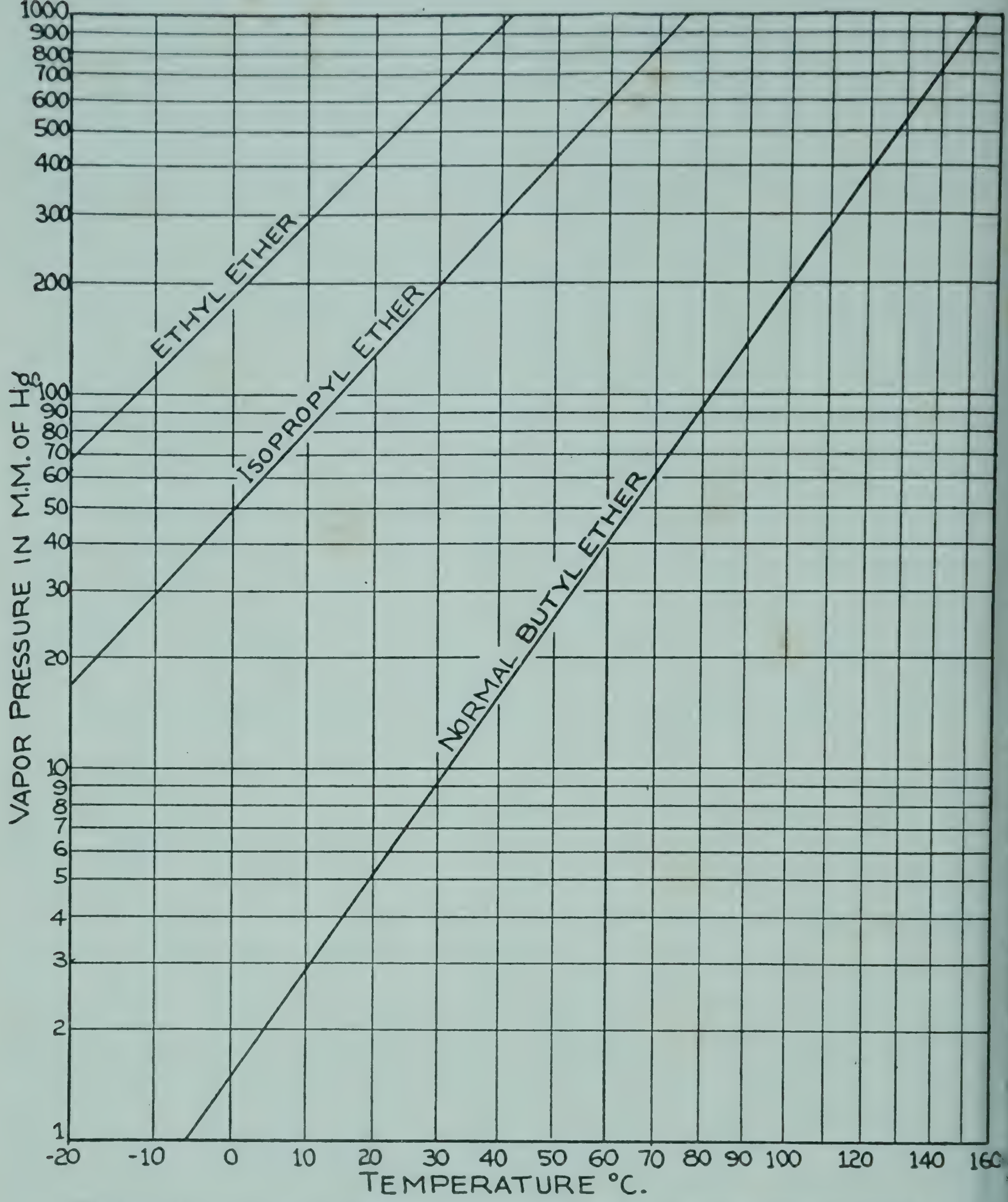


FIGURE 15.3. Vapor Pressure of Some Ethers at Various Temperatures.[2]

which, with but few improvements, is still used. It is completely miscible with ethyl alcohol and many organic solvents, but is only slightly soluble in water. It is a good solvent for many organic substances, among which are alkaloids, oils, dyes, fats, gums, resins, nitrocellulose, hydrocarbons, raw linseed oil, dewaxed dammar, rosin, ester gum, perfumes, unvulcanized rubber and smokeless powder. A mixture of ethyl ether and ethyl alcohol has excellent solvent properties for nitrocellulose, thus being used extensively in gun powder manufacture. Although ethyl ether is used as a general anesthetic in surgery, the bulk of its manufacture as shown in the war time end-use pattern below, is used as a solvent for nitrocellulose in making rayon, guncotton, collodion, and plastics. Equal to its importance as a solvent is its use as an extracting medium for alkaloids, fats, oils, vulcanized rubber, and waxes, and the extraction and concentration of acetic acid. It is employed as a reaction medium in the Grignard reaction, as a refrigerant, in Diesel fuels, and in dry cleaning. Ethyl ether, having the tendency to form peroxides that are explosive, should not be distilled before it is treated with an aqueous solution of sodium sulfite, or some other easily oxidizable material.

ALLOCATIONS OF ETHYL ETHER (ALL GRADES): MARCH 1–JUNE 30, 1945
(Thousands of pounds)

Use	*Amount*	*Per cent*
Total allocations	20,276	100.0
Direct military and export[1]	6	[2]
Other uses	20,270	100.0
Explosives	10,917	54.4
Rubber manufacture	2,459	12.1
Basic medicinals	1,723	8.5
Ethylamine	1,152	5.7
Pharmaceuticals	595	2.9
Recovery of acetic acid	247	1.2
Mimeograph stencils	242	1.2
Dyestuffs	145	0.7
Ethyl centralite	144	0.7
Leather finishes	126	0.6
Adhesives and resins	113	0.6
Denaturants	109	0.5
Shoe cleaners	63	0.3
Meat casings	48	0.2
Miscellaneous uses and small orders[3]	2,187	10.3

[1] End-use data are not available.

[2] Less than one-tenth of one per cent.

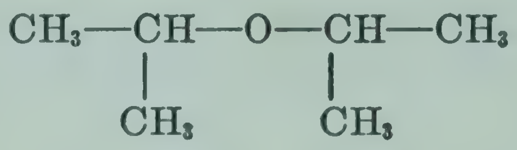
[3] Includes ether used in research and in the manufacture of miscellaneous chemicals.

Typical Properties and Specifications

Apparent ignition temperature in air		190°C
Boiling point at 760 mm		34.5°C
Coefficient of expansion		0.00164 per 1°C
Constant-boiling mixtures (% by wt.)		
Ethyl ether 99%	Carbon disulfide 1.0%	B.P. at 760 mm 34.5°C
Ethyl ether 44.5%	Methyl formate 55.5%	B.P. at 760 mm 28.2°C
Ethyl ether 98.9%	Water 1.1%	B.P. at 760 mm 34.1°C

Electrical conductivity at 25°C	4×10^{-13} recip. ohm
Explosive limits	2.34–6.15%
Flash point	−40°F
Freezing point	−116.2°C
Heat of combustion	651 Cal./mol.
Heat of vaporization	83.96 cal./g at B.P.
Refractive index at 17°C	1.3542
Specific gravity at 20/20°C	0.7146
Specific heat at 30°C	0.5476 cal./g
Surface tension at 20°C	17.0 dynes/sq cm
Solubility in water at 20°C	6.9% by wt.
Solubility of water in solvent at 20°C	1.3% by wt.
Viscosity at 20°C	0.00233 poise
Vapor pressure at 20°C	442.0 mm Hg
Weight per gallon at 20°C	5.95 lbs.
at 17°C	5.3542 lbs.
Acidity (as acetic)	0.002% by wt., max.

Isopropyl Ether



$$CH_3—\underset{\displaystyle CH_3}{\underset{|}{CH}}—O—\underset{\displaystyle CH_3}{\underset{|}{CH}}—CH_3$$

Isopropyl ether is a colorless, flammable liquid with an ethereal odor. Although its properties are quite similar to those of ethyl ether, it is in some respects a superior solvent for extraction purposes. This is because it has a higher boiling point, a lower vapor pressure and a lower solubility in water, making possible more efficient recovery of the solvent. Isopropyl ether is miscible with most organic solvents, as well as acetic acid, but it will not mix with or dissolve the ethanolamines, glycols, glycerols, and their monoacetates.

It is a valuable solvent for animal, vegetable and mineral oils and waxes. Its range of solvency for cellulose esters is increased when mixed with isopropanol. This solvent mixture is also valuable for dewaxing paraffin-base oils because by the presence of isopropanol the ether is prevented from dissolving the paraffin wax, thus permitting the mineral oil to remain in solution.

A mixture of the ether and ethanol will dissolve nitrocellulose and ethylcellulose, but not cellulose acetate. The principal use for isopropyl ether is in the concentration of dilute solutions of acetic acid and lactic acids. Watson's[3] data on the concentration of lactic acid by isopropyl ether and other solvents is shown in Table 15.1. Isopropyl ether is used to extract the active principles of glandular products, such as the sterols and nicotine from tobacco. It is a solvent for many natural and synthetic resins and is used as a textile spotting agent, in paint and varnish removers, and in rubber cements. It has been found useful as an antiknock agent in motor fuels

TABLE 15.1.—CONCENTRATION OF LACTIC ACID BY ENTRAINING LIQUIDS[3]

TOTAL ACIDITY BEFORE CONCN.	ENTRAINING LIQUID	DISTN. TEMP. RANGE (VAPOR)	PERIOD BEFORE ANALYSIS	ANALYSIS OF CONCENTRATED ACID				
				Total acidity	Lactic acid	Lactyl-lactic acid	Lactide	Water
%		°C	*Days*	%	%	%	%	%
50.00	Benzene	76–82	4	101.92	66.34	32.02		1.64
73.40	Benzene	76–79	6	104.22	60.28	39.94	0.0	0.0
			188	104.26	24.96	68.50	2.59	3.95
85.35	Benzene	78–80	5	104.55	59.13	39.95	0.86	0.06
			184	104.63	22.88	70.42	2.85	3.85
64.20	Toluene	90–108	17	106.83	13.98	79.32	4.09	2.61
86.27	Toluene[a]	100–109	13	109.21	1.04	91.25	5.62	2.09
85.35	Benzene-toluene (50–50)	87–93	4	105.01	55.93	42.81	1.25	0.01
			154	105.99	19.74	77.64	2.67	2.95
85.35	Benzene–propylene dichloride (69–31)	84 (max.)	4	104.29	61.76	38.19	0.07	0.0
			91	104.62	24.59	72.03	. .	3.38
85.35	*n*-Butyl chloride	72–78	12	104.52	43.10	54.20	0.95	1.75
			152	104.84	19.44	74.48	2.16	3.92
85.35	Isopropyl ether[b]	61–65	12	103.90	50.18	48.15	0.17	1.50
85.35	Carbon tetrachloride[c]	75–79	113	105.64	24.66	72.88		2.46
85.35	Propylene dichloride[c]	88–95	111	104.26	22.20	73.85		3.95
85.35	Trichloroethylene (tech.)[b, c]	81–85	106	104.18	26.58	69.84		3.58
26.10	Trichloroethylene (tech.)[c]	77–87	98	100.93	37.21	57.35		5.44
85.35	Chlorosol[b,c,d]	70–80	106	103.55	26.18	69.63		4.19
85.35	Tetrachloroethylene[c]	98–119	110	106.93	7.14	83.08	6.02	3.76
85.35	Methylene chloride[b,c]	39–55	112	103.88	24.28	70.83	0.76	4.13
85.35	Methyl isobutyl ketone[b]	87–116	96	105.33	20.21	76.61		3.18
85.35	Ethylene dichloride–petroleum ether (50–50)	48–79	96	104.11	25.78	70.50		3.72
85.35	Toluene–petroleum ether (25–75)	44–95	104	107.42	9.85	84.75	2.77	2.63

[a] Distillation period was 5.5 hours.

[b] Entraining liquid miscible with concd. acid.

[c] Entraining liquid heavier than water.

[d] Chlorosol is 75 per cent ethylene dichloride and 25 per cent carbon tetrachloride.

because of its high octane rating. Isopropyl ether, like ethyl ether, forms peroxides which must be destroyed before distillation. This can be done conveniently in the following manner.

Add 10 cc. of the ether to 150 cc. of 2 *N* sulfuric acid. Add 3 to 5 drops of 1 per cent ammonium molybdate solution (a catalyst to favor the liberation of iodine), and 15 cc. of 10 per cent potassium iodide solution. Shake well and allow to stand 15 minutes. Titrate the liberated iodine with 0.05

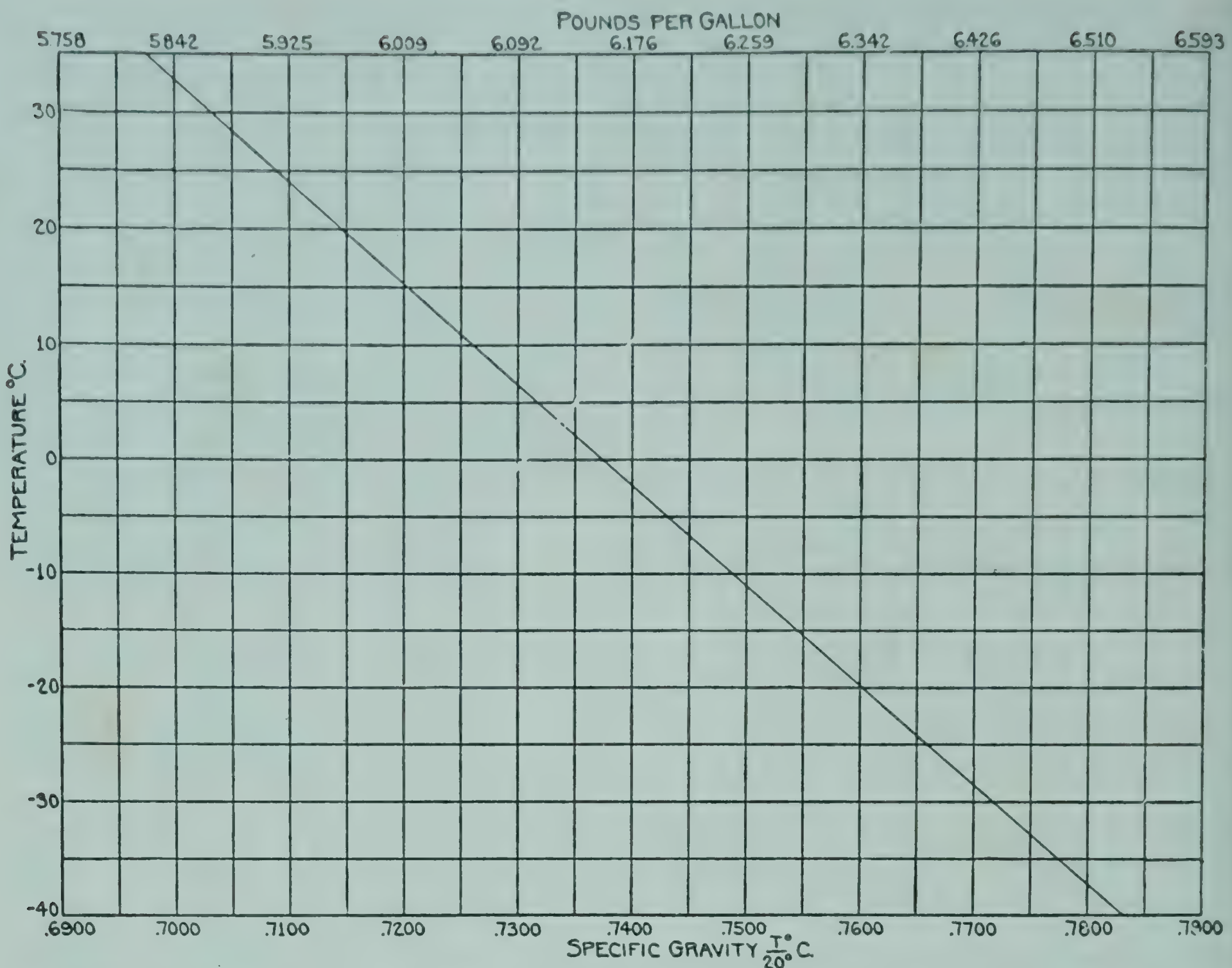


Figure 15.4. Specific Gravity and Weight per Gallon of Ethyl Ether at Various Temperatures.[1]

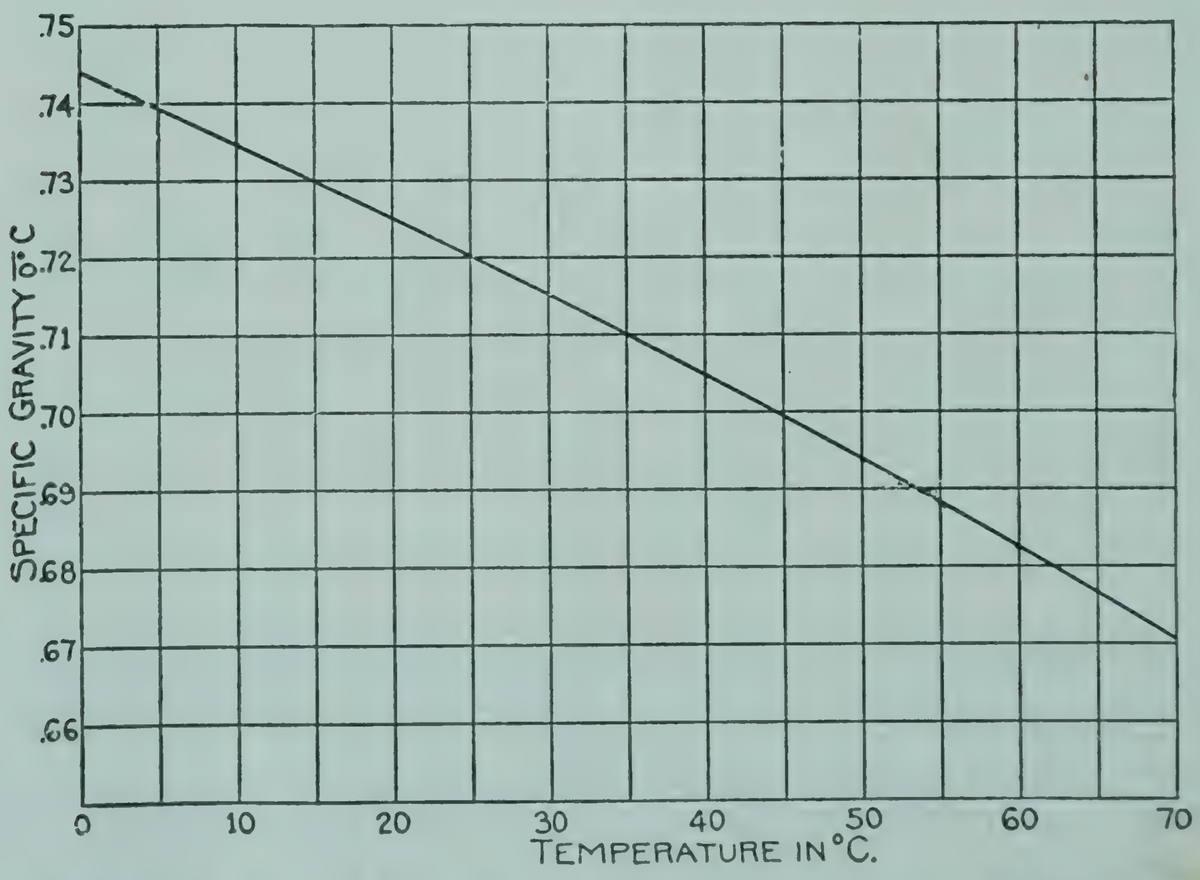


Figure 15.5. Specific Gravity and Weight per Gallon of Isopropyl Ether at Various Temperatures.[2]

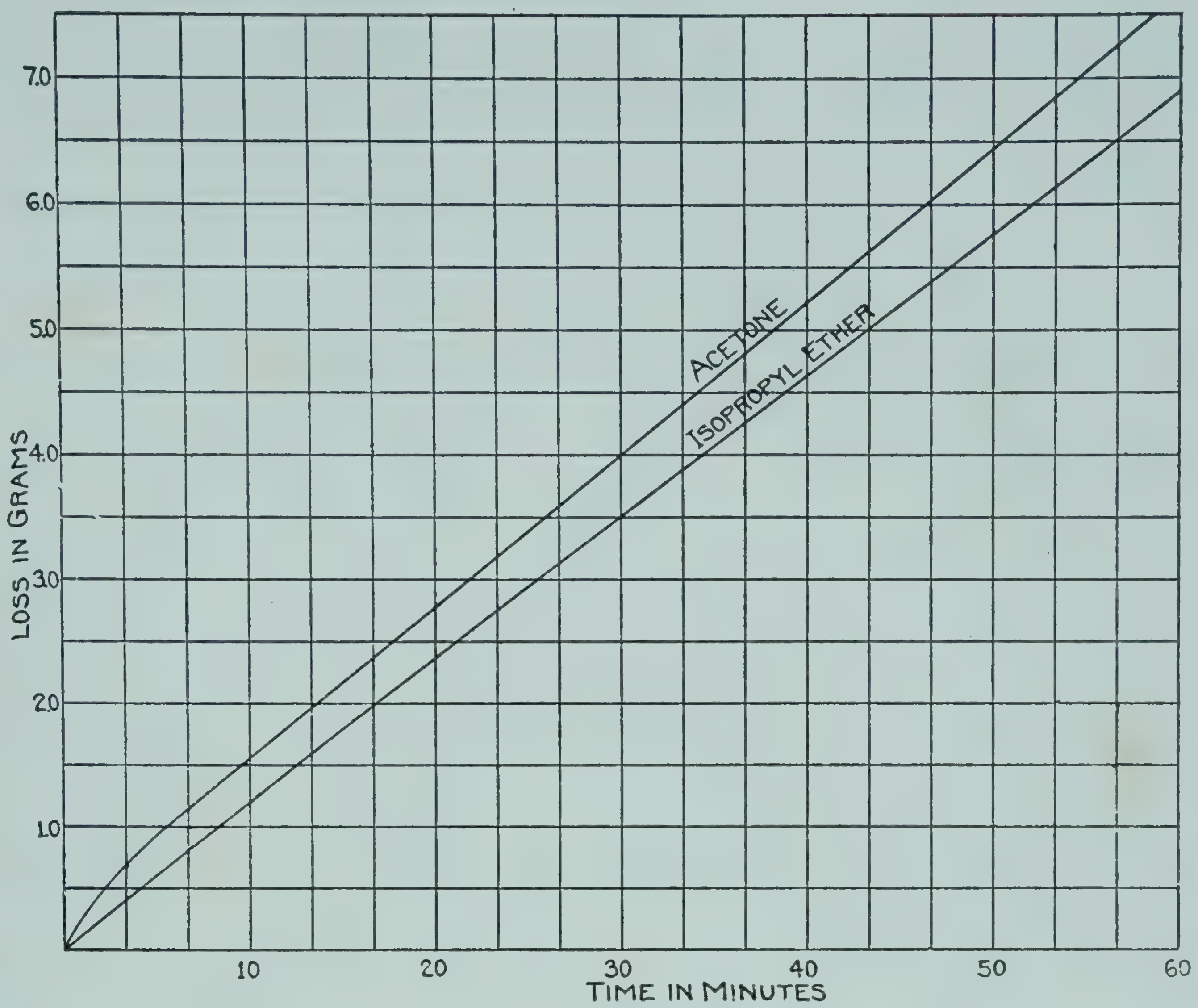


FIGURE 15.6. Evaporation Rate of Acetone and Isopropyl Ether at Room Temperature.[2]

N sodium thiosulfate and shake well after each addition. As the end point is neared, add a few cubic centimeters of starch solution as indicator and titrate until the blue color disappears.[4]

Typical Properties and Specifications

Boiling point at 760 mm	68.4°C
Coefficient of expansion	0.000828 per °F
Constant-boiling mixtures:	B.P. (°C)
Isopropyl ether with approx. 80% acetone	53.6 (739 mm)
Isopropyl ether with approx. 30% chloroform	68.5–69.5 (742 mm)
Isopropyl ether with approx. 10–15% ethanol	63 (736 mm)
Isopropyl ether with approx. 10% isopropanol	64.8–64.9 (739 mm)
Flash point (Tag closed cup)	−6°F
Freezing point	−86.8°C
Heat of combustion	16,900 Btu/lb.
Heat of fusion	25.79 cal./g
Heat of vaporization	68.2 cal./g at B.P.
Specific gravity at 20/20°C	0.7220–0.7260
Specific heat at 22–27°C	0.526 cal./g
Refractive index, 20°C	1.3681
Specific volume	151.6 cc at B.P.

Surface tension at 23°C	32 dynes/sq cm
Solubility in water at 20°C	1.2% by wt.
Solubility of water in solvent at 20°C	0.62% by wt.
Viscosity at 25°C	0.379 centipoise
Vapor pressure at 0°C	44.3 mm Hg
10	74.5
20	120.2
30	186.8
Weight per gallon at 20°C	6.08 lbs.
Acidity (as acetic)	0.005%, max.
Distillation range at 760 mm	63 to 69°C
Isopropanol content	3% by wt., max.
Residue	5 mg./100 cc

***n*-Butyl Ether** [$(CH_3CH_2CH_2CH_2)_2O$]. *n*-Butyl ether is a colorless, stable liquid, soluble in water. Having two butyl groups, this ether is an excellent solvent for many natural and synthetic resins, gums, oils, fats, organic acids, esters, and alkaloids. Beeswax and carnauba wax have limited solubility in butyl ether at room temperature, but become quite soluble at higher temperatures. *n*-Butyl ether will not dissolve cellulose acetate, benzyl cellulose, or cellulose nitrate, but when it is mixed with ethyl or butyl alcohol it becomes a solvent for ethylcellulose. Butyl ether is used as a reaction medium in organic synthesis and in the extraction and purification of essential oils, organic acids, waxes, and resins.

Typical Properties and Specifications

Boiling point at 760 mm	142.4°C
50	63
10	28
Color	Water-white
Flash point	30.6°C
Heat of vaporization	68.8 cal./g
Freezing point	Approx. −96°C
Specific gravity at 20/20°C	0.769–0.771
Refractive index at 20°C	1.3992
Surface tension at 20°C	22.9 dynes per sq cm
Solubility in water at 20°C	0.03%
Solubility of water in solvent at 20°C	0.19%
Vapor pressure at 20°C	4.8 mm Hg
Weight per gallon at 20°C	6.4 lbs
Acidity (as butyric)	0.05% by wt., max.
Distillation range	137–143°C
Water content	0.10% by wt., max.

Diamyl Ether ($C_5H_{11}OC_5H_{11}$). Commercial diamyl ether consists principally of di-*n*-amyl ether and di-isoamyl ether, with small percentages of isomeric amyl ethers and diamylene. It is a colorless to light yellow liquid

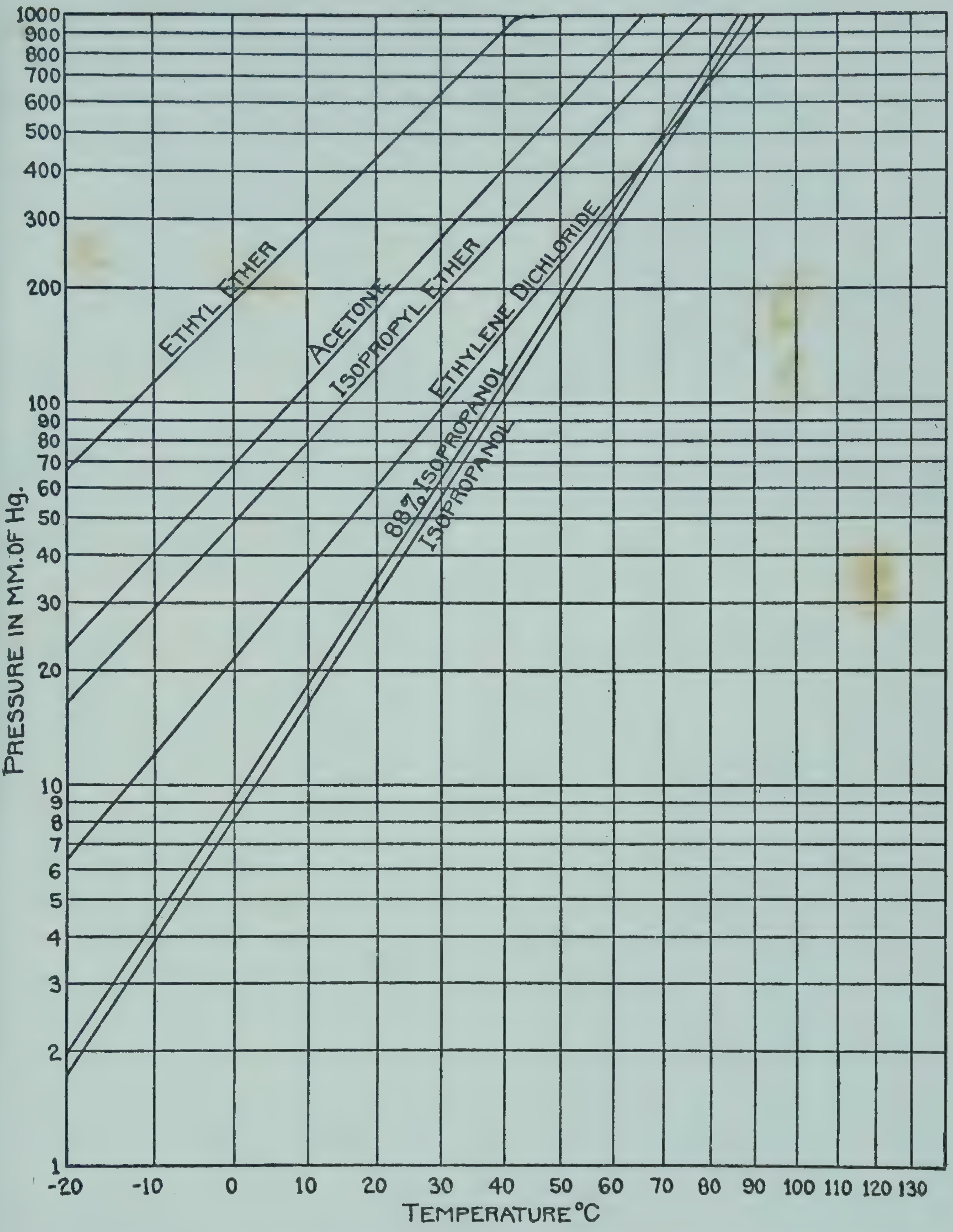


FIGURE 15.7. Vapor Pressure of Various Solvents at Different Temperatures.[2]

which is quite stable. It is insoluble in water but soluble in methanol, ethyl ether, ethyl acetate, acetone, aliphatic and aromatic hydrocarbons, fixed oils, oleic and hot stearic acids, hot paraffin and carnauba waxes, the latter two solidifying when cooled Unlike the lower aliphatic ethers, it will not dissolve nitrocellulose when admixed with ethanol. However, a mixture of diamyl ether and 20% ethanol will dissolve ethylcellulose.

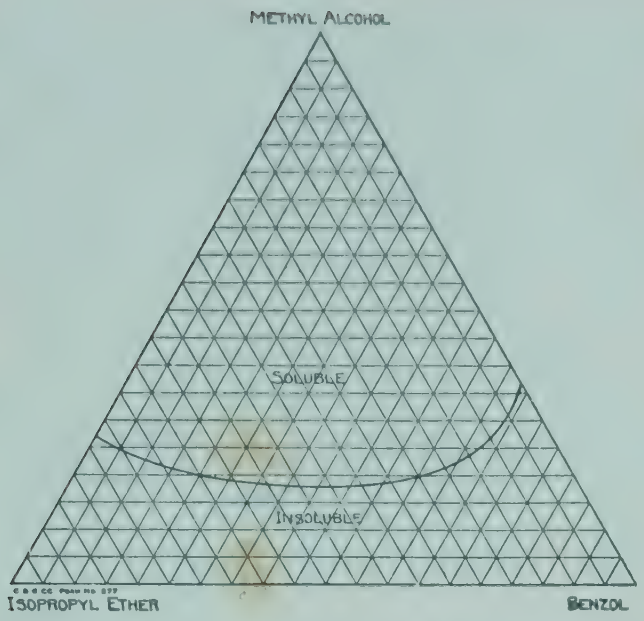


Figure 15.8. Solubility of ½-Second R. S. Nitrocellulose in Mixtures of Methyl Alcohol, Isopropyl Ether and Benzene.[2]

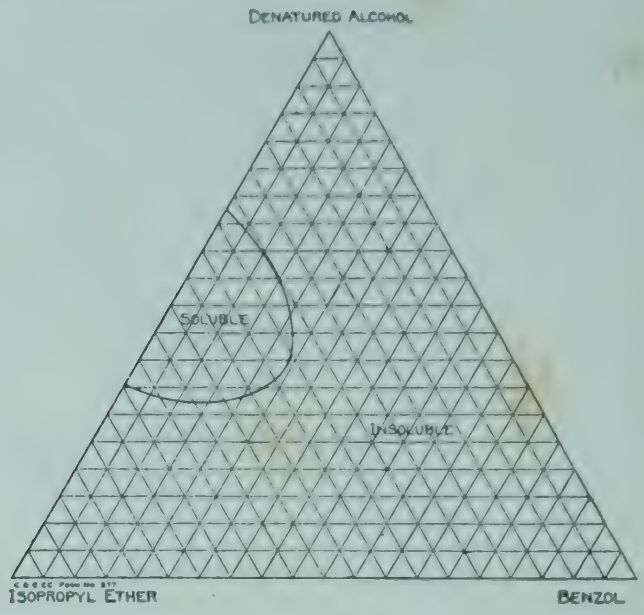


Figure 15.9. Solubility of ½-Second R.S. Nitrocellulose in Mixtures of Denatured Alcohol (C. D. No. 1), Isopropyl Ether and Benzene.[2]

Typical Properties and Specifications

Dielectric constant	3.14
Flash point (open cup)	146°F
Heat of vaporization	65.9 cal./g (calc'd)
Specific gravity at 20/20°C	0.78–0.80
Specific heat	0.513 cal/g
Refractive index at 20°C	1.4198
Surface tension at 20°C	24.8 dynes/sq cm
Freezing point	Below −75°C
Vapor pressure at 20°C	0.67 mm
Water azeotrope at 96–98°C	41% amyl ether (approx.)
Weight per gallon at 20°C	6.61 lbs
Acidity (mg. KOH per g)	0.4, max.
Distillation	
Initial boiling point	Not below 170°C
Not less than 95%	Below 200
Final boiling point	Not above 210
Water content	0.2% by wt., max.

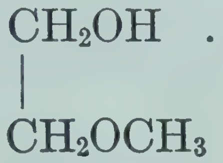
***n*-Hexyl Ether** ($C_6H_{13}OC_6H_{13}$). *n*-Hexyl ether is a colorless, stable liquid with a mild odor. It is less volatile than the lower members of the aliphatic ether group and its solubility in water is very slight. It is miscible with most organic solvents and can replace butyl ether for many similar applications. It is used as a solvent medium in chemical reactions and is a foam breaker for certain processes.

Boiling point at 760 mm	226.2°C
50	136
10	100

Flash point	170°F
Specific gravity at 20/20°C	0.7942
Solubility in water at 20°C	0.01% by wt.
Solubility of water in solvent at 20°C	0.12% by wt.
Vapor pressure at 20°C	0.07 mm Hg
Weight per gallon at 20°C	6.61 lbs.
Acidity (as acetic)	0.01% by wt., max.
Distillation range at 760 mm	205–235°C
Color (A.P.H.A.)	15 max.
Water content	0.10% by wt.

GLYCOL ETHERS

This class of compounds covers a group of nitrocellulose lacquer solvents which have attained great commercial importance over the past 20 years.

Ethylene glycol monomethyl ether (methyl "Cellosolve," methyl glycol, methoxy ethanol)  $\begin{array}{c}CH_2OH\\ |\\ CH_2OCH_3\end{array}$. A colorless, limpid, stable liquid having a mild odor, it is miscible with water, aliphatic and aromatic hydrocarbons, alcohols, ketones, glycols and most organic solvents. It is a solvent for essential oils, lignin, dammar, Elemi, ester gum, kauri, mastic, rosin, sandarac, shellac, zanzibar, nitrocellulose, cellulose acetate, alcohol-soluble dyes and many synthetic resins. Solvency for cellulose esters is augmented when a ketone or a halogenated hydrocarbon is added. The uses for methyl "Cellosolve" are as a solvent in quick-drying varnishes and enamels, in conjunction with aliphatic, aromatic and halogenated hydrocarbons, alcohols and ketones; in solvent mixtures and thinners for lacquers and dopes; in the manufacture of synthetic resin plasticizers, as a heat sealant for moisture-proof cellophane packaging material, and as a penetrating and leveling agent in dyeing processes, especially in the dyeing of leather, animal and vegetable fibers. Other uses are as a fixative in perfumes and as a solvent in odorless nail polish lacquers. Methyl "Cellosolve" should not be added to nitrocellulose lacquers containing courmarone resins or ester gum because it will cause incompatibility between these substances.

Typical Properties and Specifications

Boiling point	124.5°C (760 mm)
Specific gravity	0.9748 at $\frac{15°C}{15°C}$
Weight per gallon	8.11 lbs (15°C)
Refractive index	1.4028 (20°C)
Surface tension	35 dynes/sq cm (20°C)
Viscosity	1.6 centipoises (25°C)

Vapor pressure	7.5 mm Hg (20°C)
Specific heat	0.534 (20°–25°C)
Heat of vaporization	135 cal/g (124.5°C)
Flash-point	32°C (89.6°F)
Apparent ignition temperature in air	288°C (551°F)
Electrical conductivity	1.09×10^{-6} recip. ohm
Solubility	Miscible with water and most organic liquids

Dilution ratios
(approx. 8% cellulose ester)

	Water	Toluene	V.M. & P. Naphtha
Nitrocellulose	0.25	4.75	0.50
Cellulose acetate	0.15	1.24	0.25

TABLE 15.2.—PHYSICAL PROPERTIES OF THE MONOALKYL ESTERS OF ETHYLENE AND PROPYLENE GLYCOLS[2]

Monoalkyl Ether	Boiling point* °C.	Specific gravity 15°/15° C.	Refractive index (n_D) at 26° C.
	Ethylene Glycol		
Methyl	124.5	0.9748	1.4004
Ethyl	134.8	0.9360	1.4042 (24° C.)
Isopropyl	144.0	0.9139	1.4080
n-Propyl	150.0	0.9110	1.4125
Isobutyl	158.8	0.9130	1.4135
n-Butyl	170.6	0.9188	1.4177
Isoamyl	181.0	0.9000	1.4198
	Propylene Glycol		
Methyl	122.8	0.9335	1.4035
Ethyl	133.0	0.9090	1.4061
Isopropyl	141.5	0.8900	1.4062
n-Propyl	150.0	0.8970	1.4102
Isobutyl	161.3	0.8810	1.4112
n-Butyl	170.6	0.8890	1.4151
Isoamyl	183.3	0.8835	1.4182

*Boiling point of monoalkyl ethers of ethylene glycol at 743 mm. pressure, of propylene glycol at 736 mm.

"Cellosolve" (Ethylene Glycol Monoethyl Ether) ($C_2H_5OCH_2CH_2OH$). "Cellosolve"[2] is a colorless liquid, with a mild and agreeable odor. It has a powerful solvent action on nitrocellulose and alkyd resins and an extremely high dilution ratio with coal-tar hydrocarbons. This solvent will tolerate 4.9 times its own volume of toluene before the mixture will cease to dissolve nitrocellulose, while butyl acetate will tolerate only 2.9 times its volume.

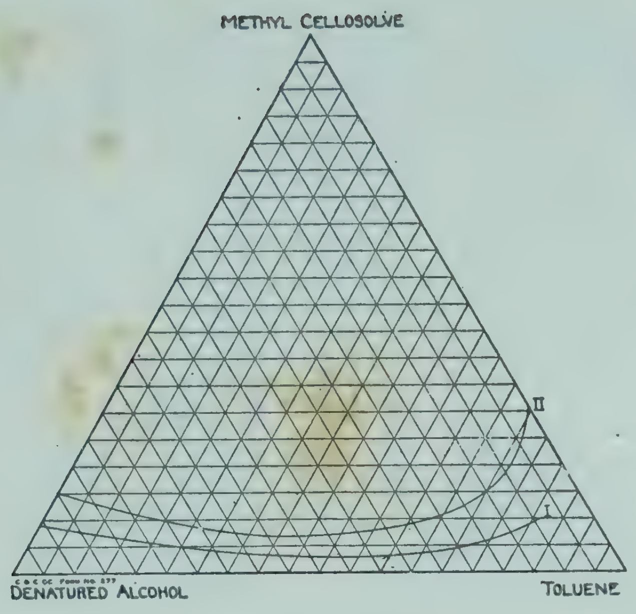


FIGURE 15.10. Solubility of ½-Second R.S. Nitrocellulose in Mixtures of Methyl "Cellosolve," Denatured Alcohol and Toluene. I denotes solution commences, II a 10% solution easily made.[2]

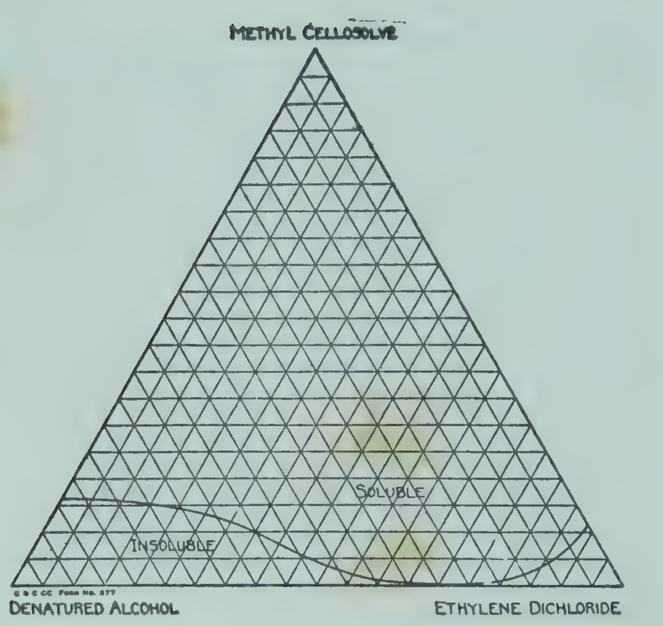
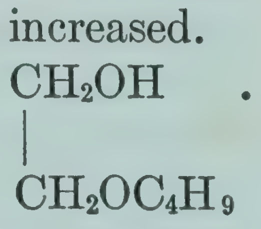


FIGURE 15.11. Solubility of ½-Second R.S. Nitrocellulose in Mixtures of Methyl "Cellosolve," Denatured Alcohol and Ethylene Dichloride.[2]

"Cellosolve" is widely used in the manufacture of lacquers and dopes, where its use is a distinct advantage in that the last portion of the solvent mixture to evaporate remains a good solvent for the non-volatile ingredients, and gives a clear, homogeneous film. Its high dilution ratios permit the preparation of excellent lacquers and lacquer thinners at low cost by the use of a large amount of non-solvent. "Cellosolve" differs from the more commonly used lacquer solvents and should not be substituted directly for another solvent in a particular formula. Best results will be obtained by taking advantage of its outstanding features and formulating the lacquer around them. High grade lacquers which meet the strictest requirements as to performance may be formulated with "Cellosolve."

In addition to its use in lacquers, "Cellosolve" is being used in varnish removers, cleaning solutions, dyeing, and in textile printing. In leather finishing with water pigments and dye solutions, "Cellosolve" gives increased penetration, better flow, and prevents a spotty finish. When used with various dyes in the printing or dyeing of textiles it increases the solubility of the dye, giving brighter shades and faster colors. Its use as a mutual solvent in the formulation of soluble fatty oils is also of importance. Being soluble in water and certain fatty oils, more rapid dispersion of the oil in water is obtained and the stability of the emulsion is increased.

Ethylene Glycol Mono-*n*-Butyl Ether (butyl "Cellosolve")



$$\begin{array}{l} CH_2OH \\ | \\ CH_2OC_4H_9 \end{array}.$$

A colorless liquid of mild odor and low volatility. It is a solvent for practically all resins, except the Bakelite type, and for nitrocellulose and some

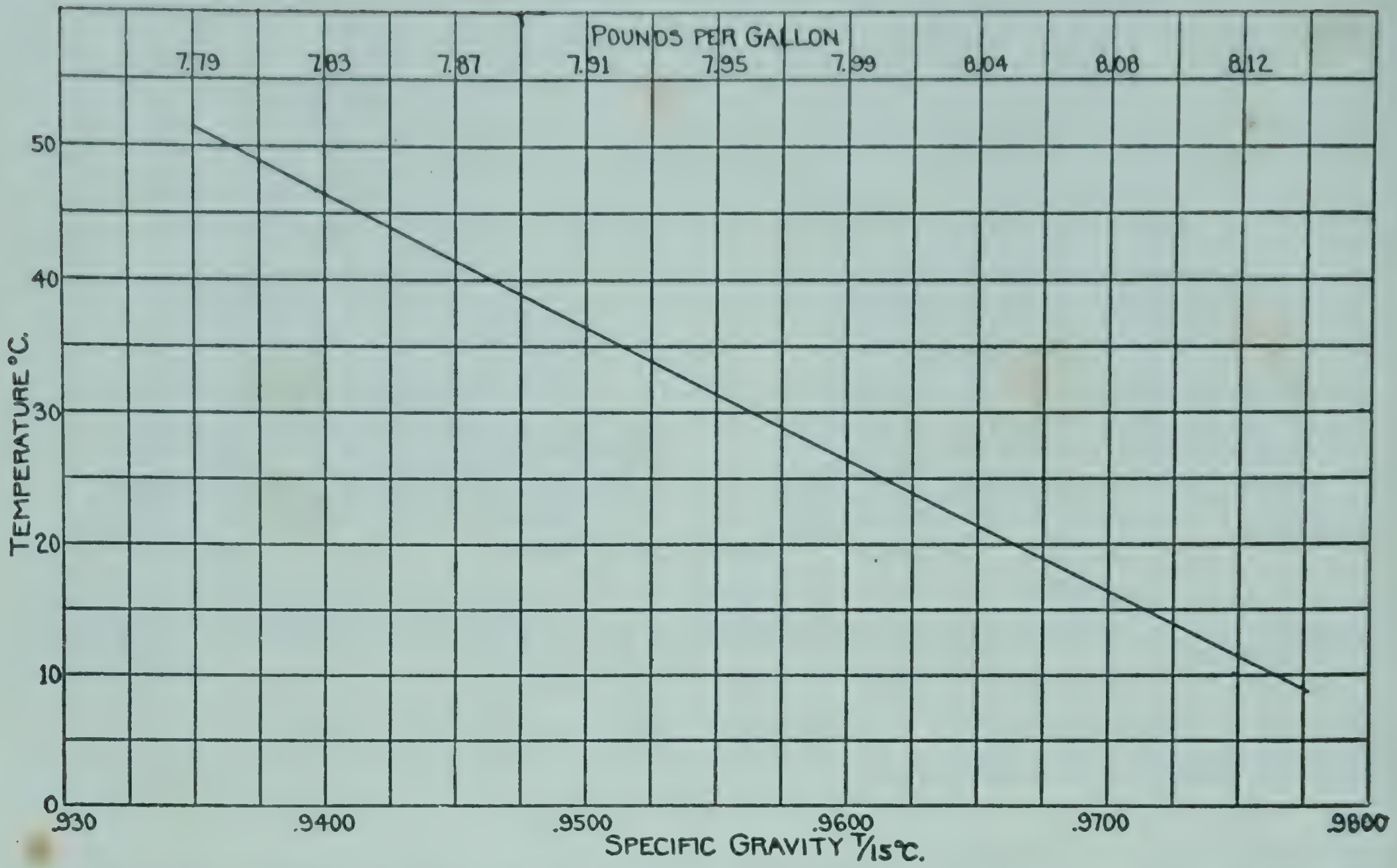


FIGURE 15.12. Specific Gravity and Weight per Gallon of Methyl "Cellosolve" at Various Temperatures.[2]

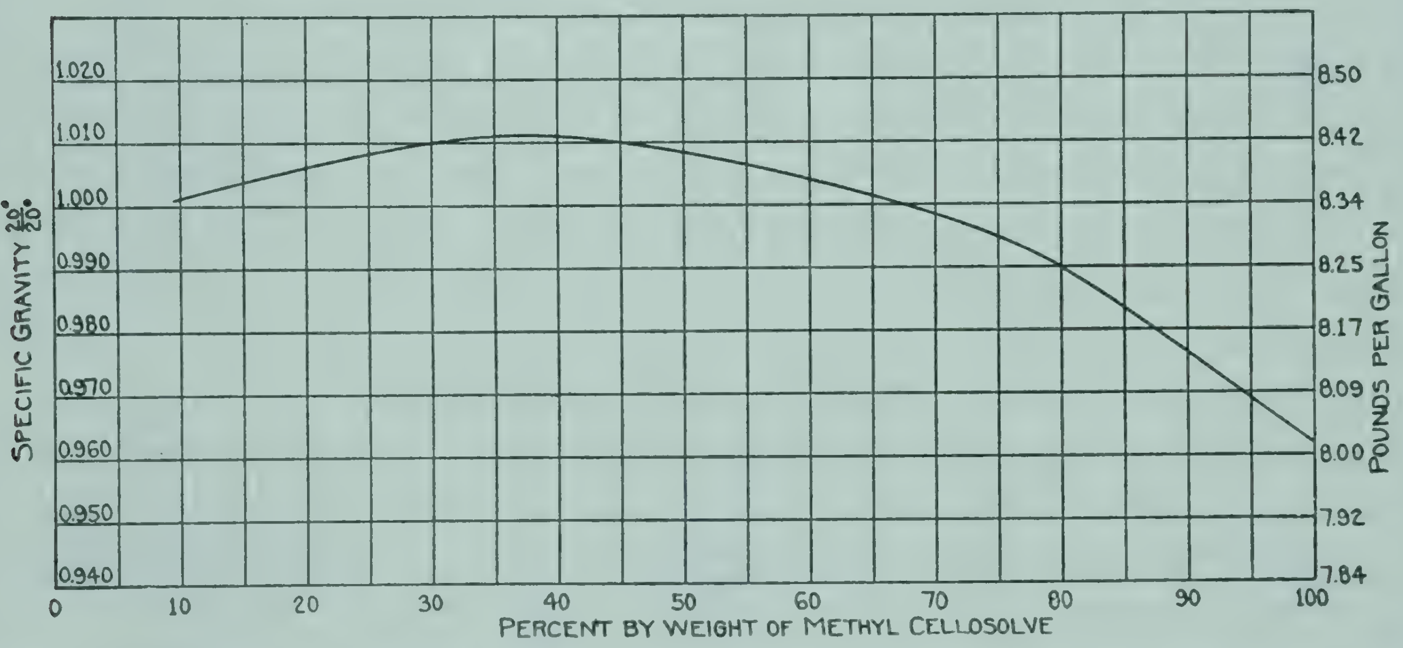


FIGURE 15.13. Specific Gravity and Weight per Gallon of Aqueous Solutions of Methyl "Cellosolve."[2]

types of cellulose ethers its solvency is rather slow. Owing to its high boiling point, low rate of evaporation, and strong solvent powers, it is the last portion of the solvent mixture to leave the film thereby promoting good flowout and clear, homogeneous films. It is used in nitrocellulose dipping lacquers, brushing compositions, in dry-cleaning compounds and in varnish removers. It is also used as a thinner either alone or in combination with petroleum hydrocarbons where rapid drying is not essential and

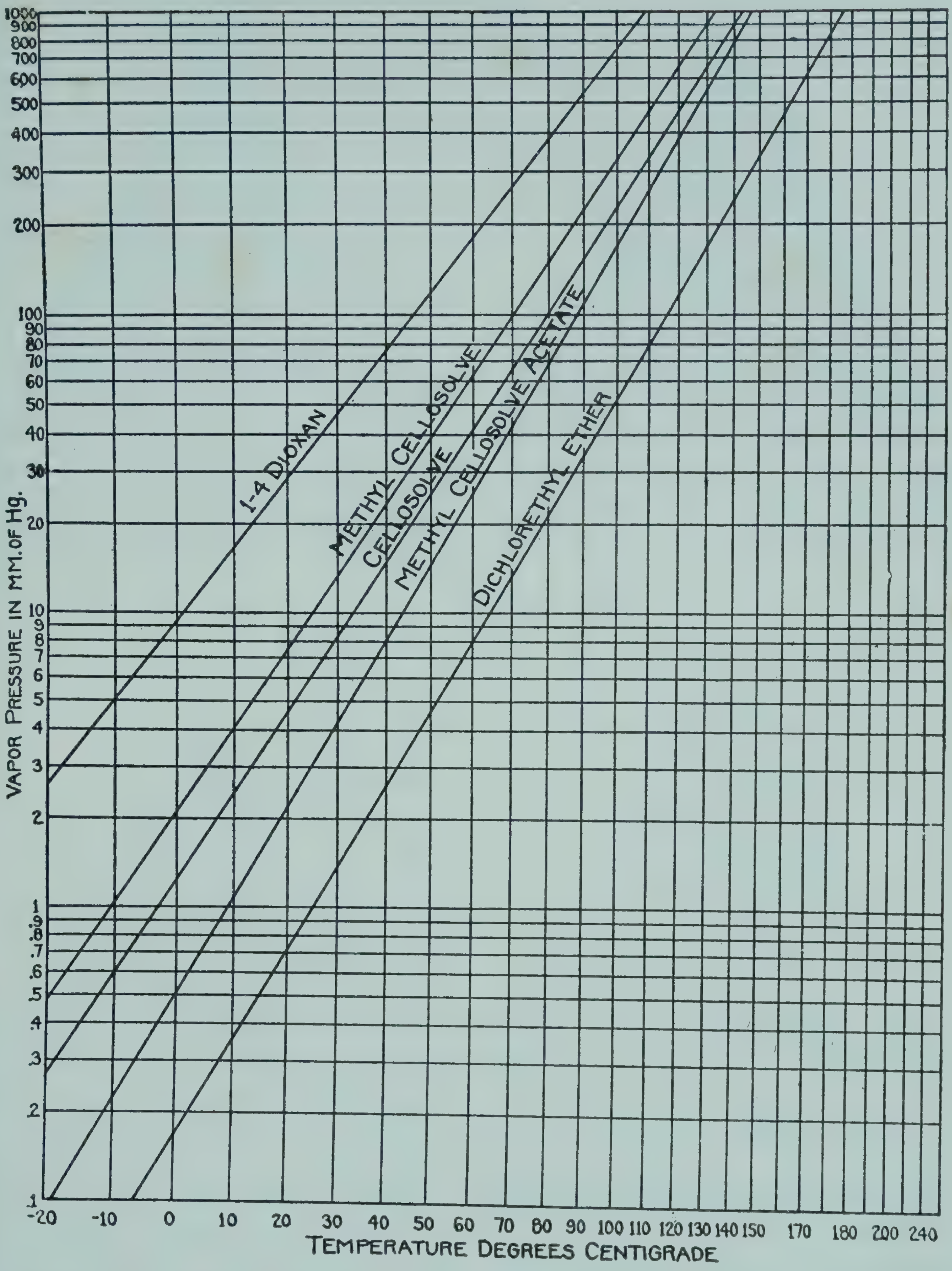
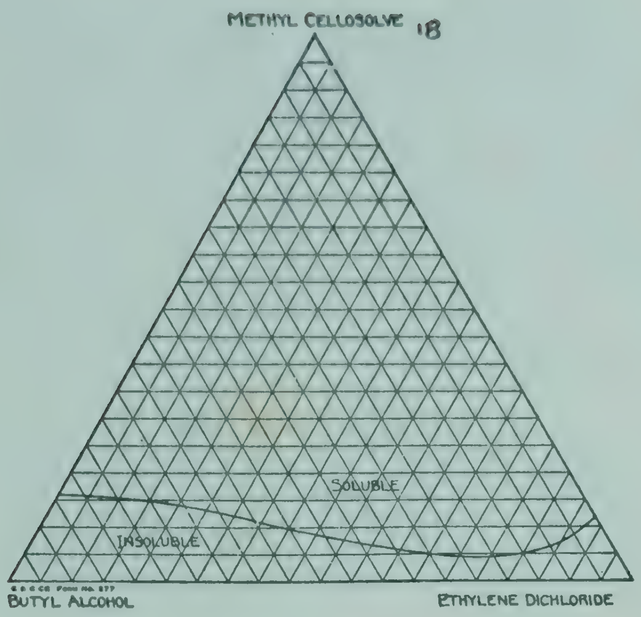


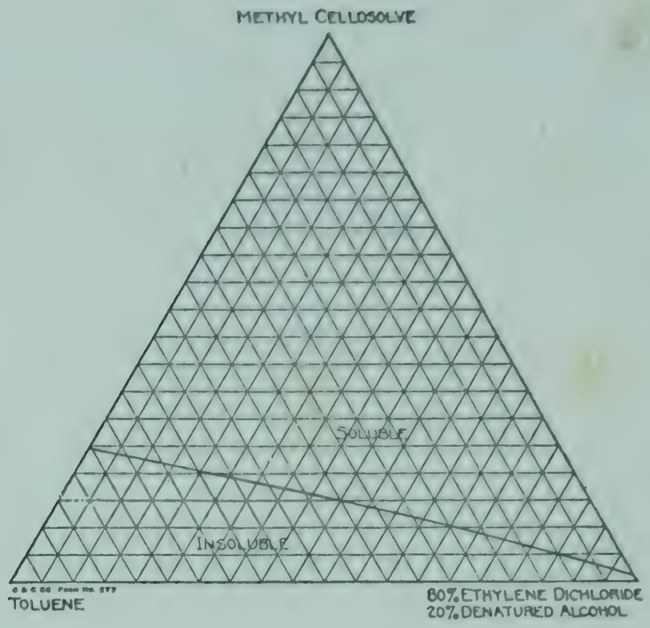
FIGURE 15.14. Vapor Pressures of Various Solvents at Different Temperatures.[2]

where anti-skinning is desired. Butyl "Cellosolve" is utilized commercially in the manufacture of soluble oils, hydraulic brake fluids and synthetic resin plasticizers.

Molecular weight	118.11
Boiling point	170.6°C



15.15. Solubility of ½-Second R. S. Nitrocellulose in Mixtures of Methyl "Cellosolve," Butyl Alcohol and Ethylene Dichloride.[2]

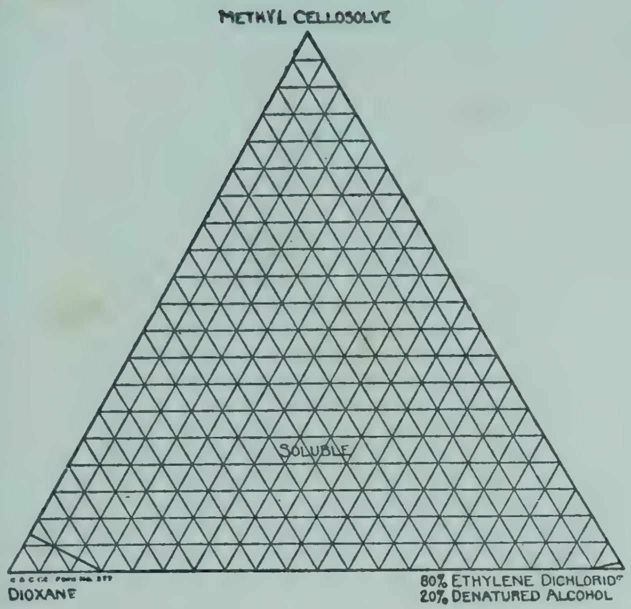


15.16. Solubility of ½-Second R. S. Nitrocellulose in Mixtures of Methyl "Cellosolve," Toluene and 80% Ethylene Dichloride + 20% Denatured Alcohol.[2]

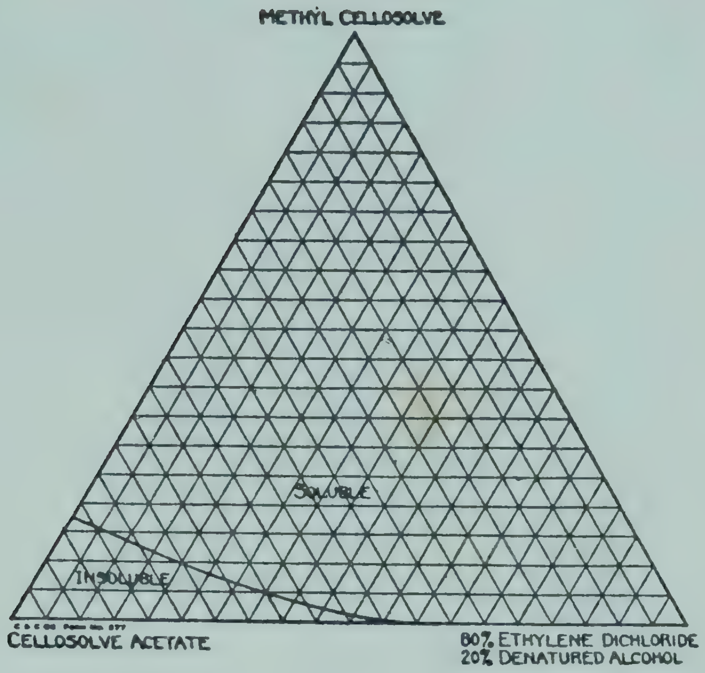
Specific gravity	0.9188 at $\frac{15°C}{15°C}$
Weight per gallon	7.65 (15°C)
Refractive index	1.4190 (25°C)
Surface tension	31.5 dynes/sq. cm. (25°C)
Viscosity	3.318 centipoises (25°C)
Vapor pressure	0.12 mm Hg (20°C)
Specific heat	0.583
Flash point	60.5°C. (141°F)
Solubility	Miscible with most organic liquids
Dilution ratios	Toluene 3.5 V.M. & P. naphtha 2.2 Final concentration ½-sec. R.S. nitrocellulose solution, approx. 8%
Electrical conductivity	0.432 × 10^{-6} recip. ohm

Ethylene Glycol Monophenyl Ether (Phenyl "Cellosolve," "Dowanol" 1[5]) ($C_6H_5OCH_2CH_2OH$). Phenyl "Cellosolve" is a colorless, water immiscible liquid with a faint rose-like odor. Having both the structure of benzene and ethanol it is a good solvent for a large number of industrial substances. It is used principally as a perfume fixative in cosmetics and soaps. It may also be used in organic synthesis to prepare intermediates useful as germicides and plasticizers.

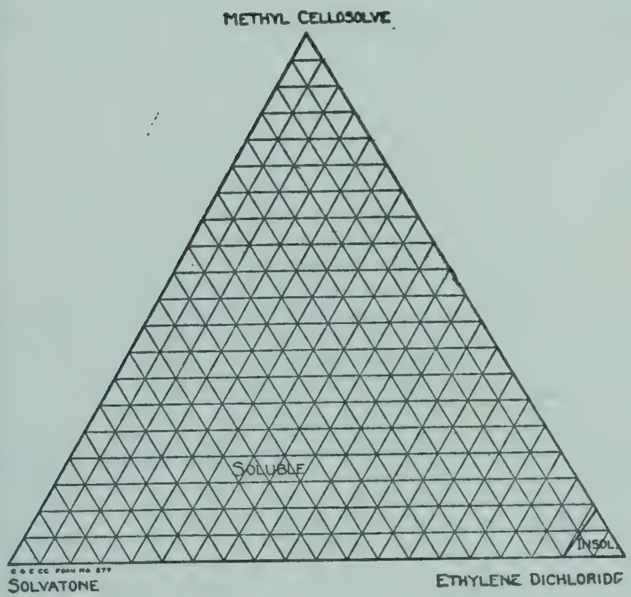
Distillation range at 760 mm	240–248°C
Flash point	250°F
Specific gravity at 20/20°C	1.1094



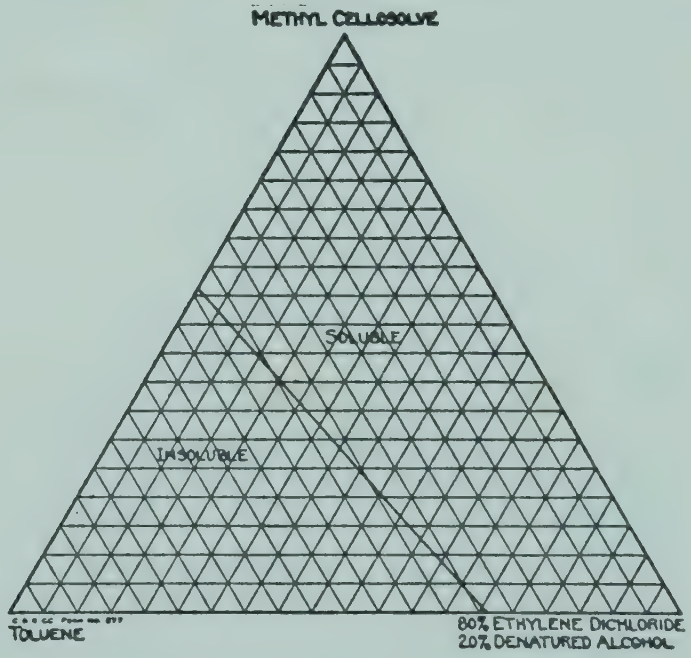
15.17. Solubility of ½-Second R. S. Nitrocellulose in Mixtures of Methyl "Cellosolve," 1-4 Dioxane and 80% Ethylene Dichloride + 20% Denatured Alcohol.[2]



15.18. Solubility of Low Viscosity Cellulose Acetate in Mixtures of Methyl "Cellosolve," "Cellosolve" Acetate and 80% Ethylene Dichloride + 20% Denatured Alcohol.



15.19. Solubility of Low Viscosity Cellulose Acetate in Mixtures of Methyl "Cellosolve," Solvatone and Ethylene Dichloride.[2] (Solvatone—80% Acetone, 10% Isopropanol, 10% toluene.)



15.20. Solubility of Low Viscosity Cellulose Acetate in Mixtures of Methyl "Cellosolve," Toluene, and 80% Ethylene Dichloride + 20% Denatured Alcohol.[2]

Freezing point	−2°C
Refractive index at 25°C	1.535
Fire point	129°C
Viscosity at 25°C, centipoises	20.7
at 60°C, centipoises	4.4
Solubility in water at 20°C	2.7% by wt
Solubility of water in solvent at 20°C	10.8% by wt
Vapor pressure at 20°C	0.03 mm Hg
Weight per gallon at 20°C	9.23 lbs

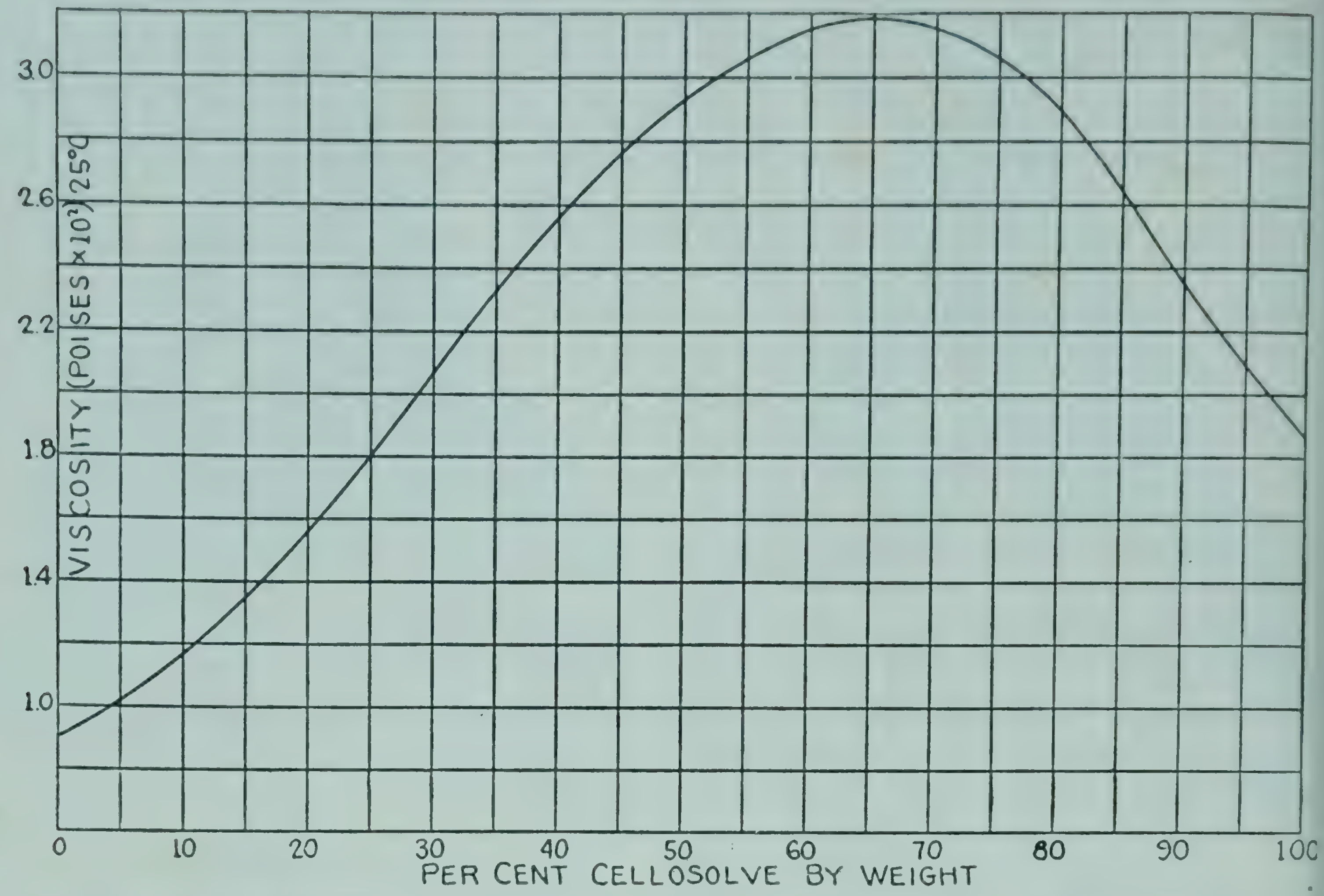


FIGURE 15.21. Viscosity of Aqueous Solutions of "Cellosolve" (99%) at 25°C.[2]

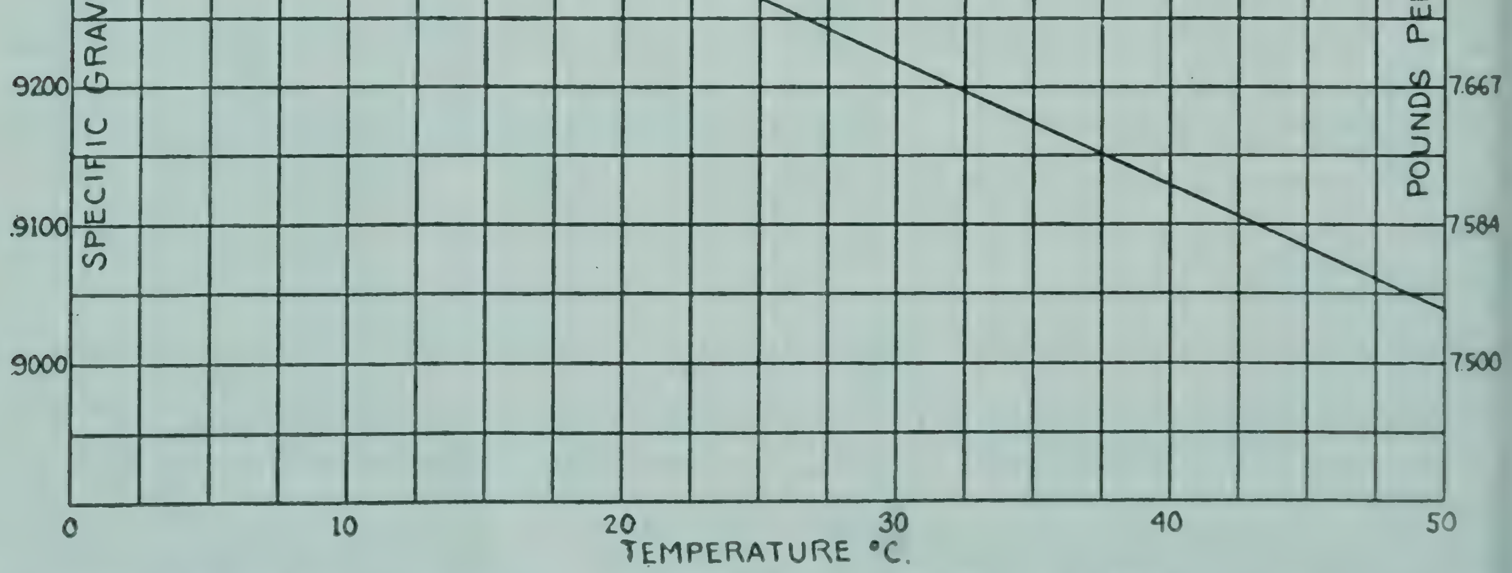


FIGURE 15.22. Specific Gravity and Weight per Gallon of "Cellosolve" (99%) at Various Temperatures.[2]

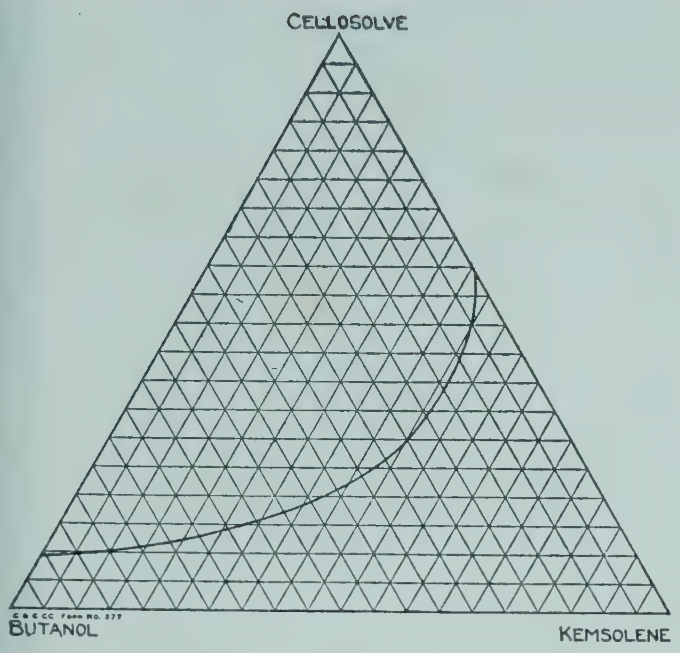


FIGURE 15.23. Solubility of ½-Second R. S. Nitrocellulose in Mixtures of "Cellosolve," Butanol and Kemsolene.[2]

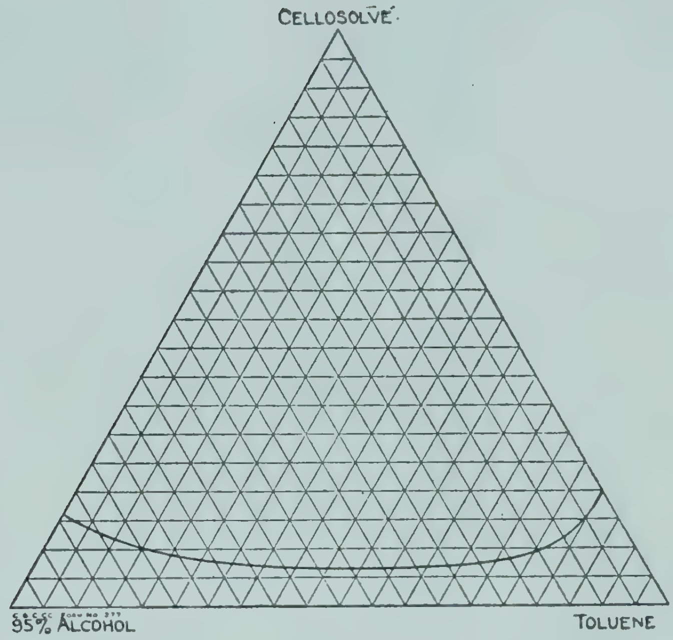


FIGURE 15.24. Solubility of ½-Second R. S. Nitrocellulose in Mixtures of "Cellosolve," 95% Alcohol and Toluene.

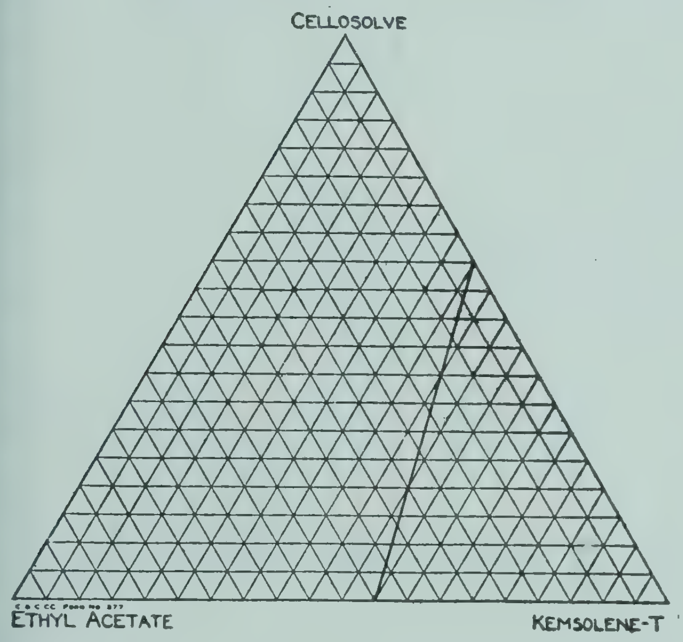


FIGURE 15.25. Solubility of ½-Second R. S. Nitrocellulose in Mixtures of "Cellosolve," Ethyl Acetate and Kemsolene T.

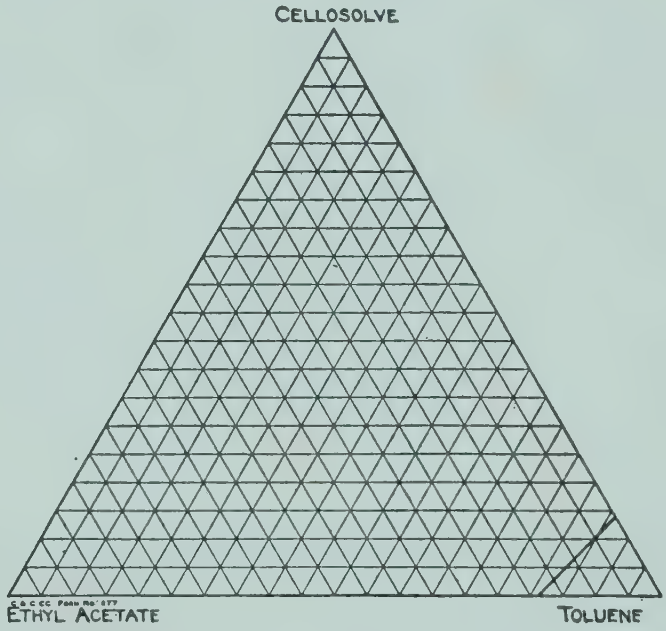


FIGURE 15.26. Solubility of ½-Second R. S. Nitrocellulose in Mixtures of "Cellosolve," Ethyl Acetate and Toluene.

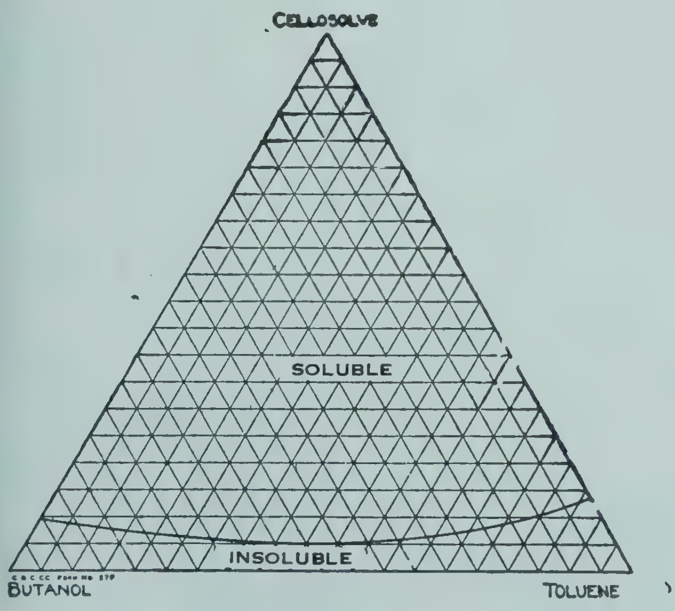


FIGURE 15.27. Solubility of ½-Second R. S. Nitrocellulose in Mixtures of "Cellosolve," Butanol, and Toluene.[2]

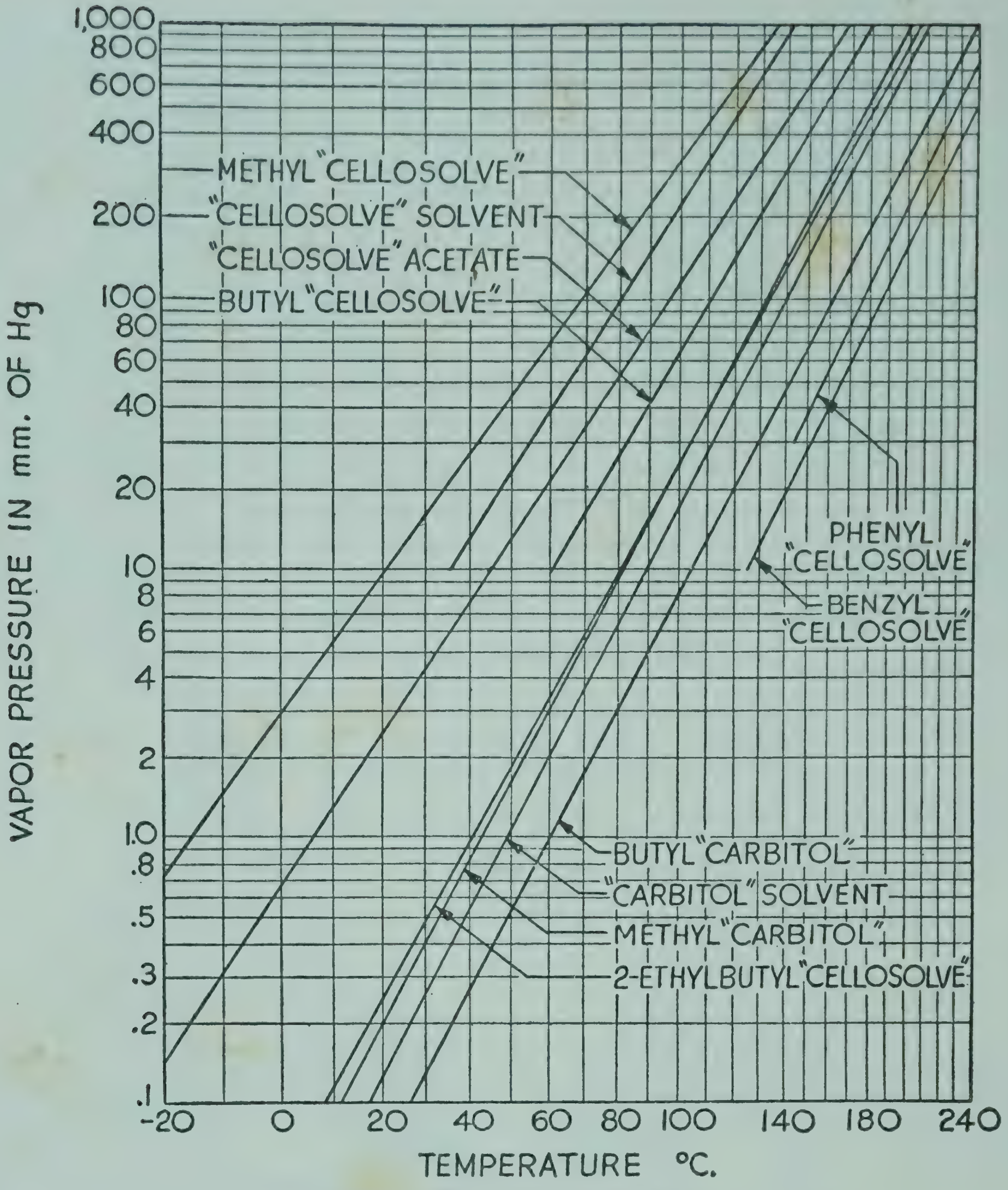


FIGURE 15.28. Vapor Pressures.

Ethylene Glycol Monobenzyl Ether (Benzyl "Cellosolve") ($C_6H_5CH_2$-OCH_2CH_2OH). Benzyl "Cellosolve" is a water-white liquid which will dissolve a large number of organic substances among which are oils, fats, greases, some vinyl resins, dewaxed dammar, rosin, ester gum, etc. It is used principally as a high-boiling solvent in lacquers, in inks, and in textile dyeing.

Acidity (as acetic)	0.010% by wt, max
Boiling point at 760 mm	255.9°C
Distillation range at 760 mm	248–260°C
Flash point	265°F
Specific gravity at 20/20°C	1.0670–1.0720
Solubility in water at 20°C	0.4% by wt
Solubility of water in benzyl "Cellosolve" at 20°C	18% by wt
Vapor pressure at 20°C	0.02 mm Hg
Weight per gal at 20°C	8.90 lbs

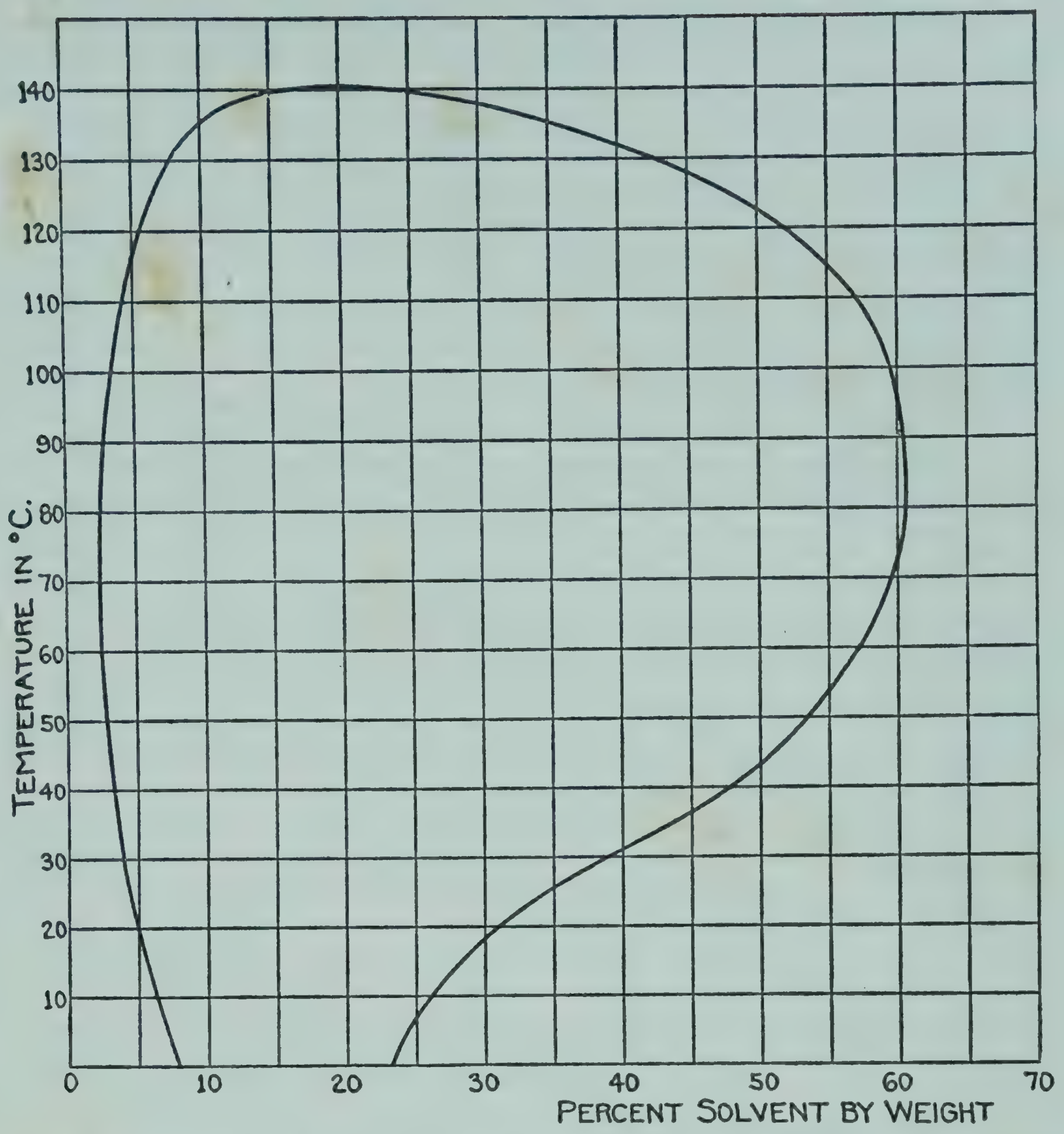


FIGURE 15.29. Solubility of Butyl "Cellosolve" in Water at Various Temperatures.[2]

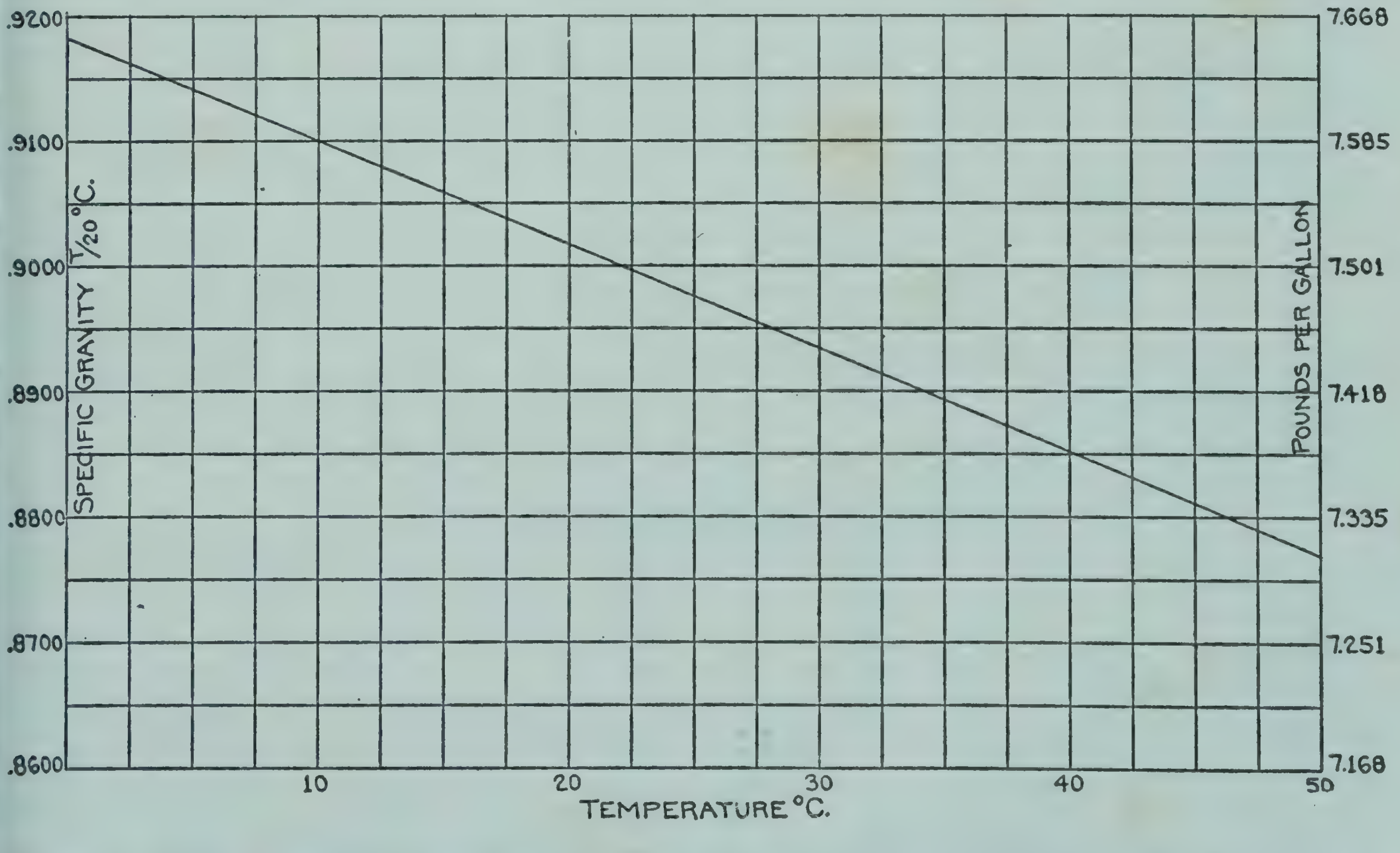


FIGURE 15.30. Specific Gravity and Weight per Gallon of Butyl "Cellosolve" at Various Temperatures.

TABLE 15.3.—FURNITURE LACQUERS FORMULATION[2]

	Pounds			
½-Second nitrocellulose	17	17	17	17
Dibutyl phthalate	3	3	3	3
50% Shellac solution		16	8	
40% Kauri solution				5
50% Resin solution			8	8
Standard dammar solution	18			

TABLE 15.4.—AUTOMOBILE LACQUER FORMULATION[2]

	Pounds				
½-Sec. nitrocellulose (dry basis)	12	12	12	12	12
Dibutyl phthalate	3	3	3	3	3
Blown castor oil (viscosity about 100 to 200 poises)	3	3	3	3	3
50% Ester gum solution (in complete mixed solvent)	6				
50% Elemi solution		6			
40% Pontianac solution (in alcohol)			8		
40% Kauri solution (in alcohol)				8	
Standard dammar solution					10
Solvent, gallons	10	10	10	10	10
Solvent Composition, per cent by Volume					
Toluene	70	65	20	20	70
Ethyl alcohol	5		60	60	5
Ethyl acetate	15	15	10	10	15
Butyl alcohol		10			
"Cellosolve"	5	10	10	10	5
"Cellosolve" acetate	5				5

TABLE 15.5.—LEATHER LACQUER FORMULATION[2]

"Dope" cotton, 15 to 20 seconds, pounds	12	12	12	12
Castor oil, pounds	6–10	6–10	6–10	6–10
Solvent (see below), gallons	10	10	10	10
Solvent Composition, per cent by Volume				
Benzene	65	35		
Toluene		30		35
Petrol (80–130°C)			50	25
Alcohol	10	10	20	20
Ethyl acetate	15	15	20	20
"Cellosolve"	10	10	10	10

TABLE 15.6.—BRUSHING LACQUER FORMULATION[2]

	POUNDS				
½-Second nitrocellulose (wet basis, 30% alcohol)	17	21	20	17	17
Blown castor oil				8	
Dibutyl phthalate	8	7	8	3	6
Dammar solution		50	25		
50% Elemi solution	12				
50% Ester gum solution (made in complete brushing lacquer solv.			15		
40% Kauri solution (in alcohol)					30
Solvent, gallons	10	10	10	10	10
Solvent Composition, per cent by Volume					
Petrol (80–130°C)	40	40		40	
Xylene (10°C)	15				
Alcohol		20		20	12
Butyl alcohol	10		15		10
Ethyl acetate	15	15	10	20	15
"Cellosolve"	15	25	10	20	15
Butyl "Cellosolve"	5		15		
Turpentine			10		40
Mineral spirit (subst. turpentine)			40		

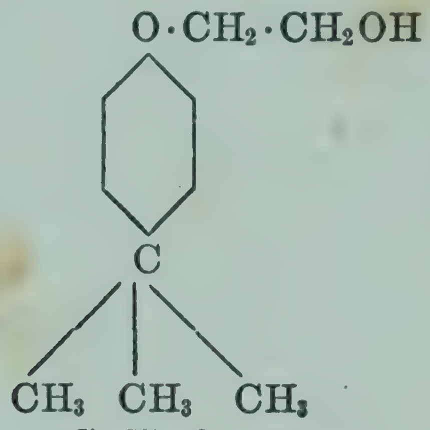
TABLE 15.7.—COMPOSITION OF HIGH-GLOSS LACQUERS[2]

	POUNDS		
½-Second nitrocellulose (wet basis)	17	17	17
Dibutyl phthalate	5	4	4
Castor oil		4	
Dammar solution	50		36
Ester gum solution		20	16
Elemi solution		20	
Solvent, gallons (approx.)	5	6	5
Solvent Composition, per cent by Volume			
Toluene	30	60	70
Petrol (180–130°C)	30		
Alcohol	10		5
Ethyl acetate (85%)	15	10	15
"Cellosolve"	15	5	5
"Cellosolve" acetate		5	5
Butyl alcohol		20	

TABLE 15.8.—COMPOSITION OF LACQUER THINNERS[2]

	PER CENT BY VOLUME		
Toluene	70		70
Petrol (80–130°C)		65	
Alcohol	5	5	5
Ethyl acetate	15	20	15
"Cellosolve"			5
"Cellosolve" acetate	10	10	5

"Dowanol" 4[5] (Ethylene glycol, p-tert-butylphenyl ether) (2-(p-tert-Butylphenoxy)ethanol)



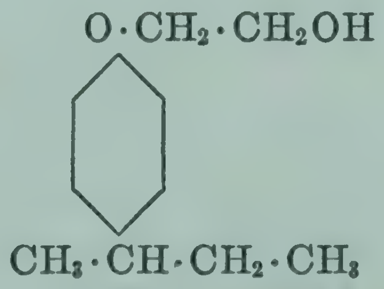
$C_{12}H_{22}O_2 = 194.3$

"Dowanol" 4 is a light yellow liquid with a faint pleasant odor.

Boiling range at 10 mm Hg, 5–95%	154–177°C
Specific gravity at 25/25°C	1.014
Freezing point	12.9°C*
Refractive index at 25°C	1.515
Flash point	120°C
Fire point	150°C
Viscosity at 38°C, centipoises	42
at 60°C, centipoises	11.6

* Freezing point of pure compound.

"Dowanol" 3[5] (Ethylene glycol, p-sec-butylphenyl ether) (2-(p-sec-Butylphenoxy) ethanol)



$C_{12}H_{18}O_2 = 194.3$

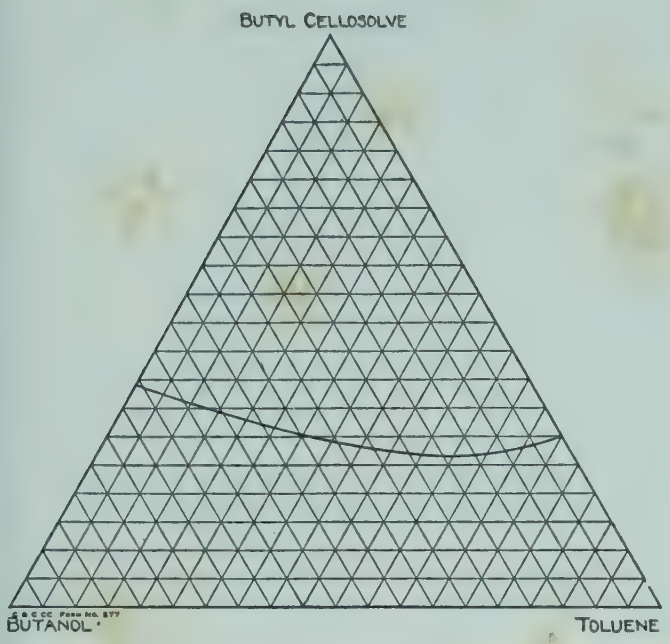


FIGURE 15.31. Solubility of ½-Second R. S. Nitrocellulose in Mixtures of Butyl "Cellosolve," Butanol and Toluene.[2]

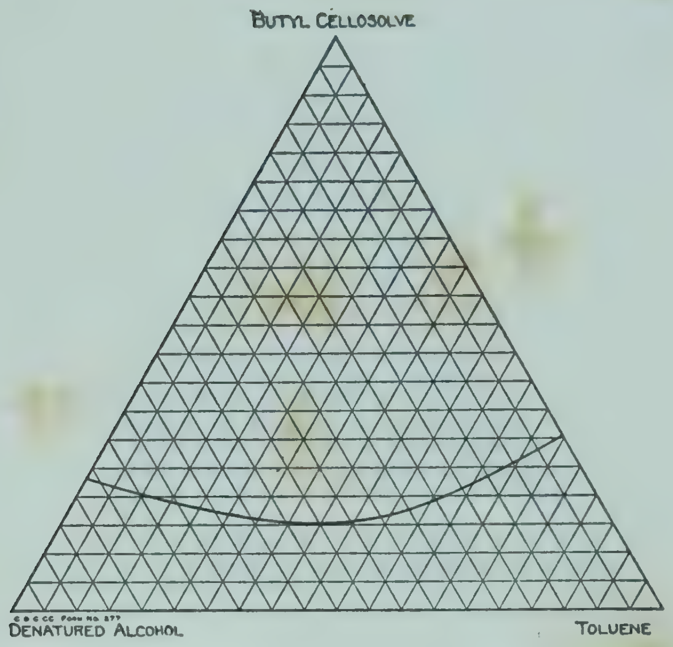


FIGURE 15.32. Solubility of ½-Second R. S. Nitrocellulose in Mixtures of Butyl "Cellosolve," Denatured Alcohol and Toluene.[2]

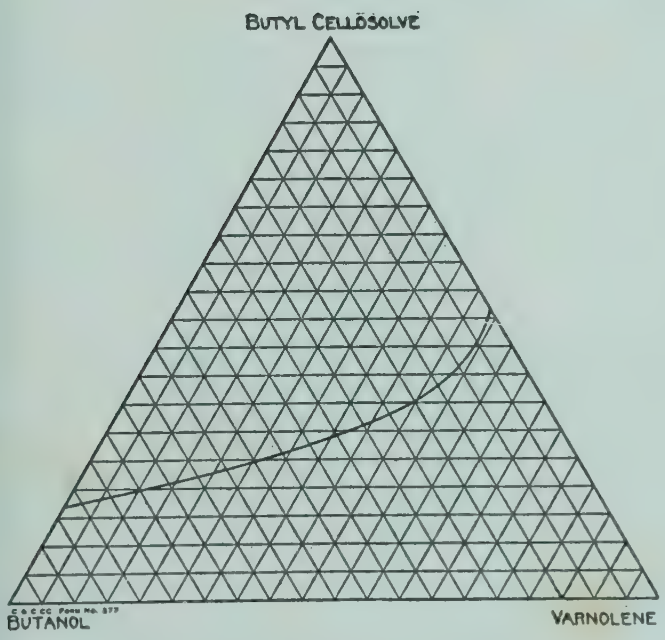


FIGURE 15.33. Solubility of ½-Second R. S. Nitrocellulose in Mixtures of Butyl "Cellosolve" Butanol and Varnolene.[2]

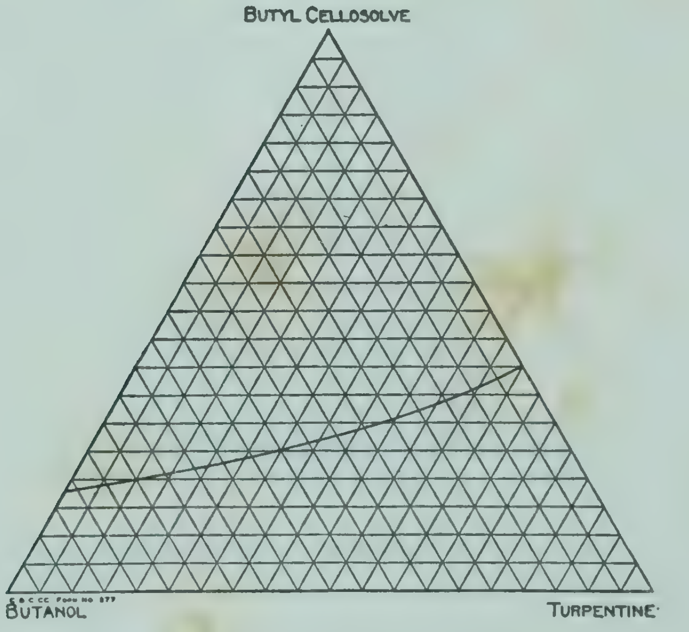


FIGURE 15.34. Solubility of ½-Second R. S. Nitrocellulose in Mixtures of Butyl "Cellosolve," Butanol and Turpentine.[2]

Typical Properties and Specifications

Boiling range at 10 mm Hg, 5–95%	156–161°C
Specific gravity at 25/25°C	1.008
Freezing point	Does not crystallize at −20°C
Refractive index at 25°C	1.514
Viscosity at 25°C, centipoises	64.6
at 60°C, centipoises	8.83

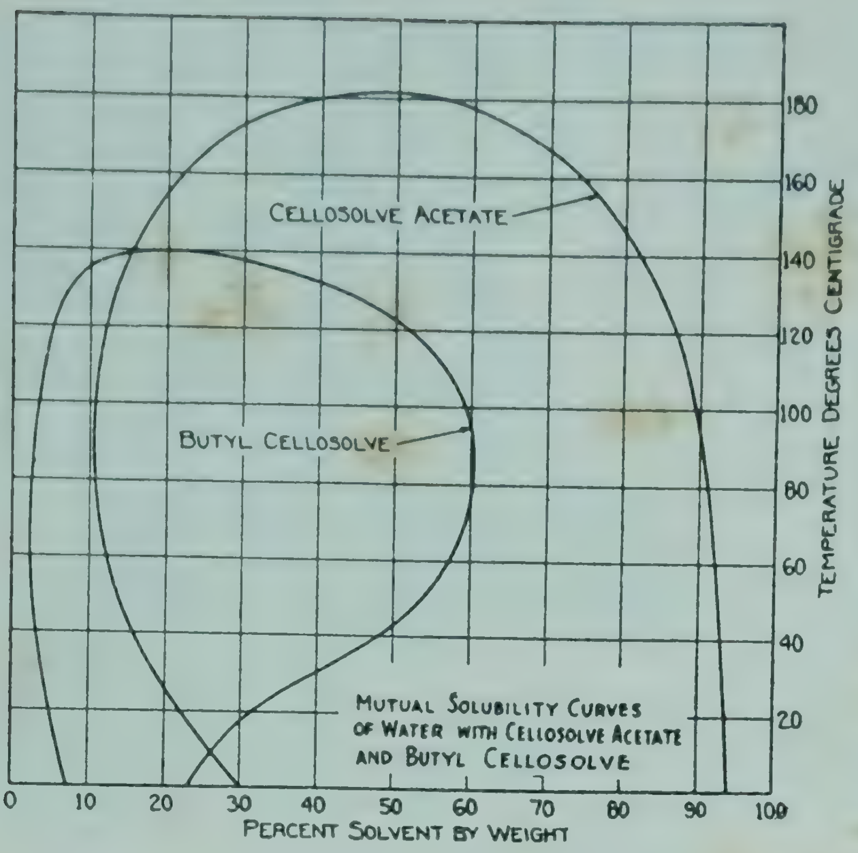


FIGURE 15.35. Mutual Solubility Curves of Water with "Cellosolve" Acetate and Butyl "Cellosolve."[2]

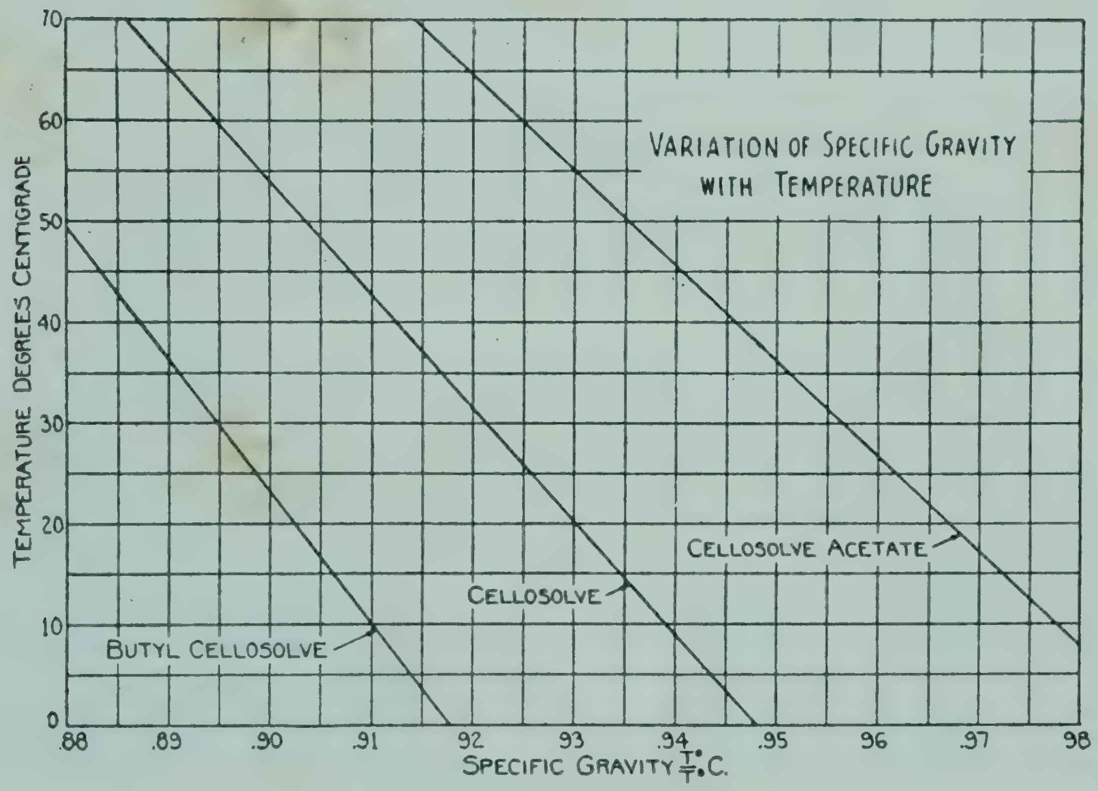


FIGURE 15.36. Variation of Specific Gravity of "Cellosolves" with Temperature.[2]

"CARBITOL" SOLVENTS

Diethylene Glycol Monomethyl Ether (methyl "Carbitol") ($CH_3OCH_2CH_2OCH_2CH_2OH$). A water-white, stable, hygroscopic liquid of agreeable odor, completely miscible with most organic solvents and water. It is a solvent for dyes, oils, fats, waxes, many natural and synthetic resins, nitrocellulose and cellulose acetate. It is used as a high-boiling solvent for printing inks and pastes, and in lacquers and synthetic resin coatings.

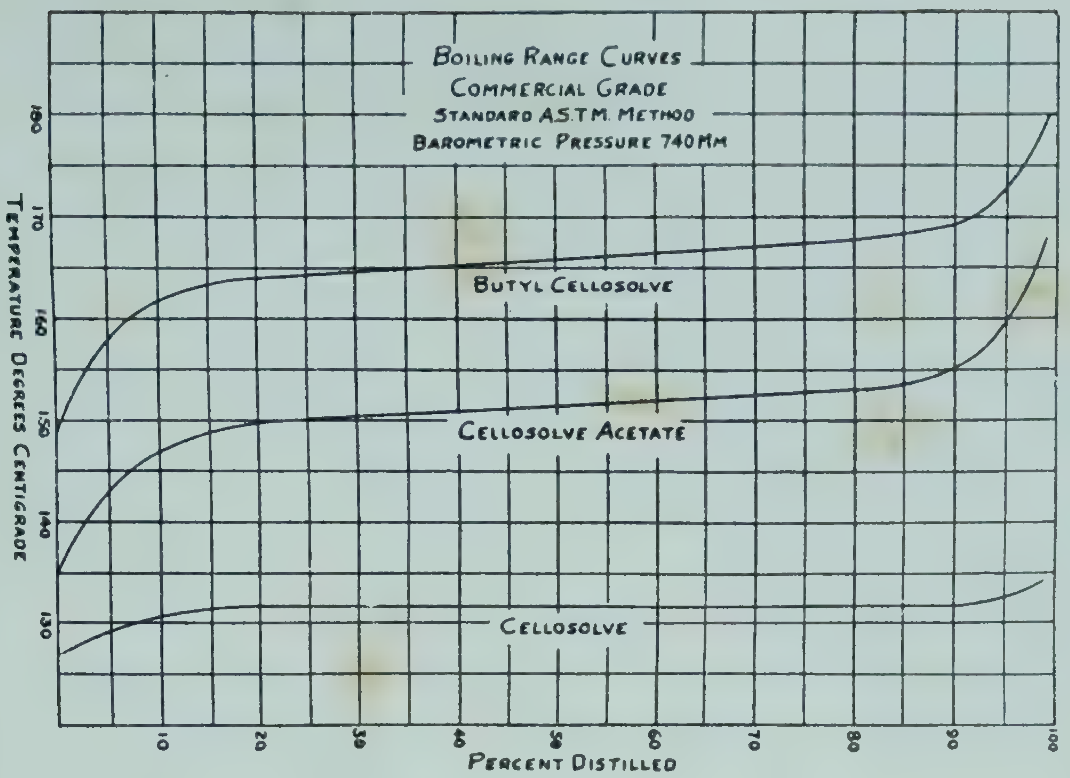


FIGURE 15.37. Boiling Range of "Cellosolves."[2]

Physical Properties

Molecular weight	120.1
Boiling point	193.2°C
Specific gravity	1.0354 at $\frac{20°C}{20°C}$
Weight per gallon	8.62 lb. (20°C)
Refractive index	1.4264 (27°C)
Surface tension	41.3 dynes/cm (25°C)
Viscosity	0.0605 poise (20°C)
Vapor pressure	0.19 mm Hg (20°C)
Specific heat	0.514 cal/g (23°C)
Heat of vaporization	90.70 cal/g at b.p.
Flash point	93°C (200°F) (ASTM open cup)
Solubility in water	Complete
Toluene dilution ratio	2.3

Diethylene Glycol Monoethyl Ether ("Carbitol") ($C_2H_5OCH_2CH_2OCH_2CH_2OH$). Diethylene Glycol Monoethyl Ether is a water-white, stable, hygroscopic liquid of a mild, pleasant odor. It is completely miscible with water and most of the commonly known organic solvents. Owing to the fact that it contains an ether, alcohol and hydrocarbon group in the molecule, it has the power to dissolve a wide variety of substances, some of which are oils, fats, waxes, dyes, camphor, natural resins like copal, kauri, mastic, rosin, sandarac, shellac and several types of synthetic resins. "Carbitol" is used as a solvent in synthetic resin coating compositions, and in lacquers, where high-boiling solvents are desired. It is used in safety

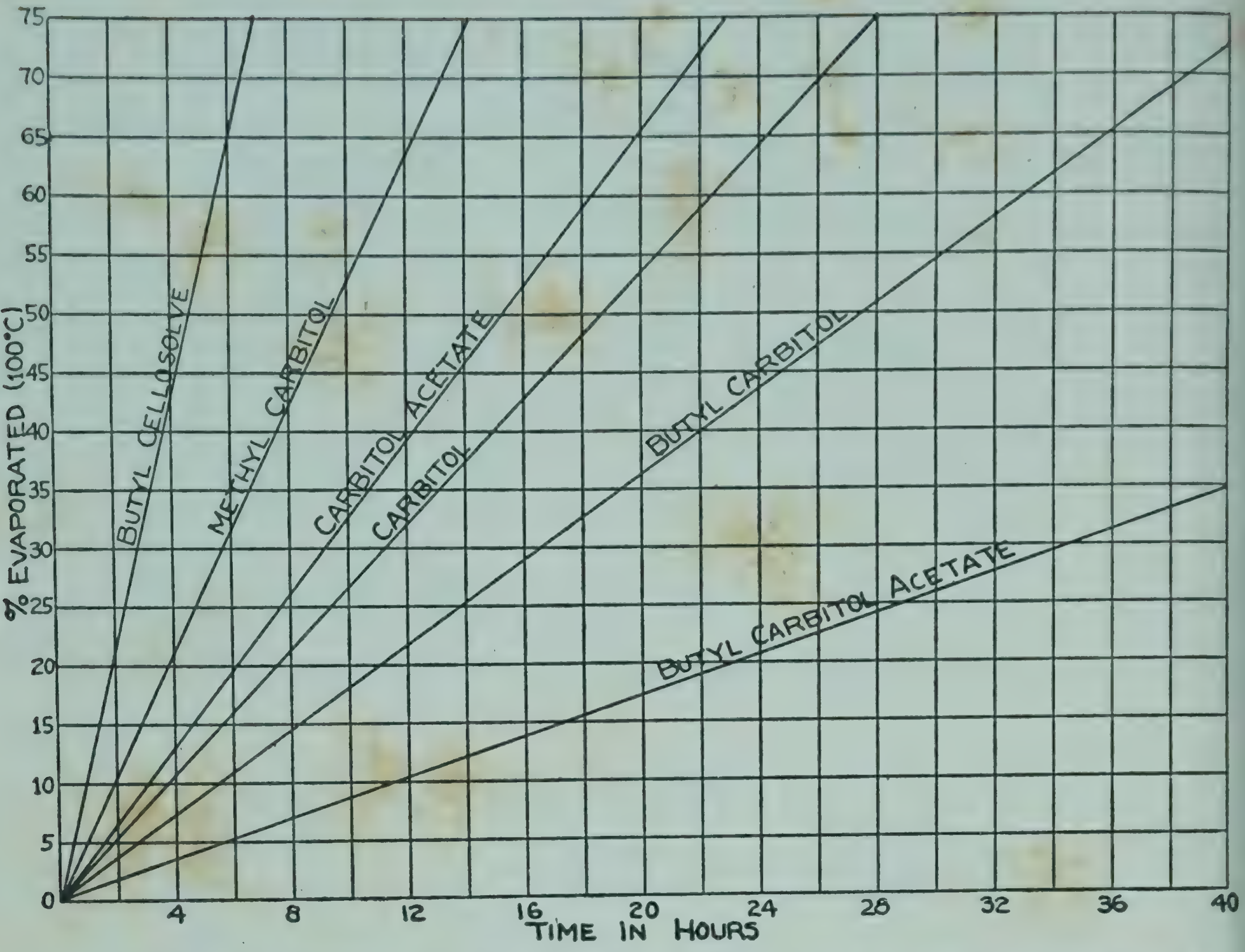


FIGURE 15.38. Evaporation Rate of Various Solvents at Room Temperature.[2]

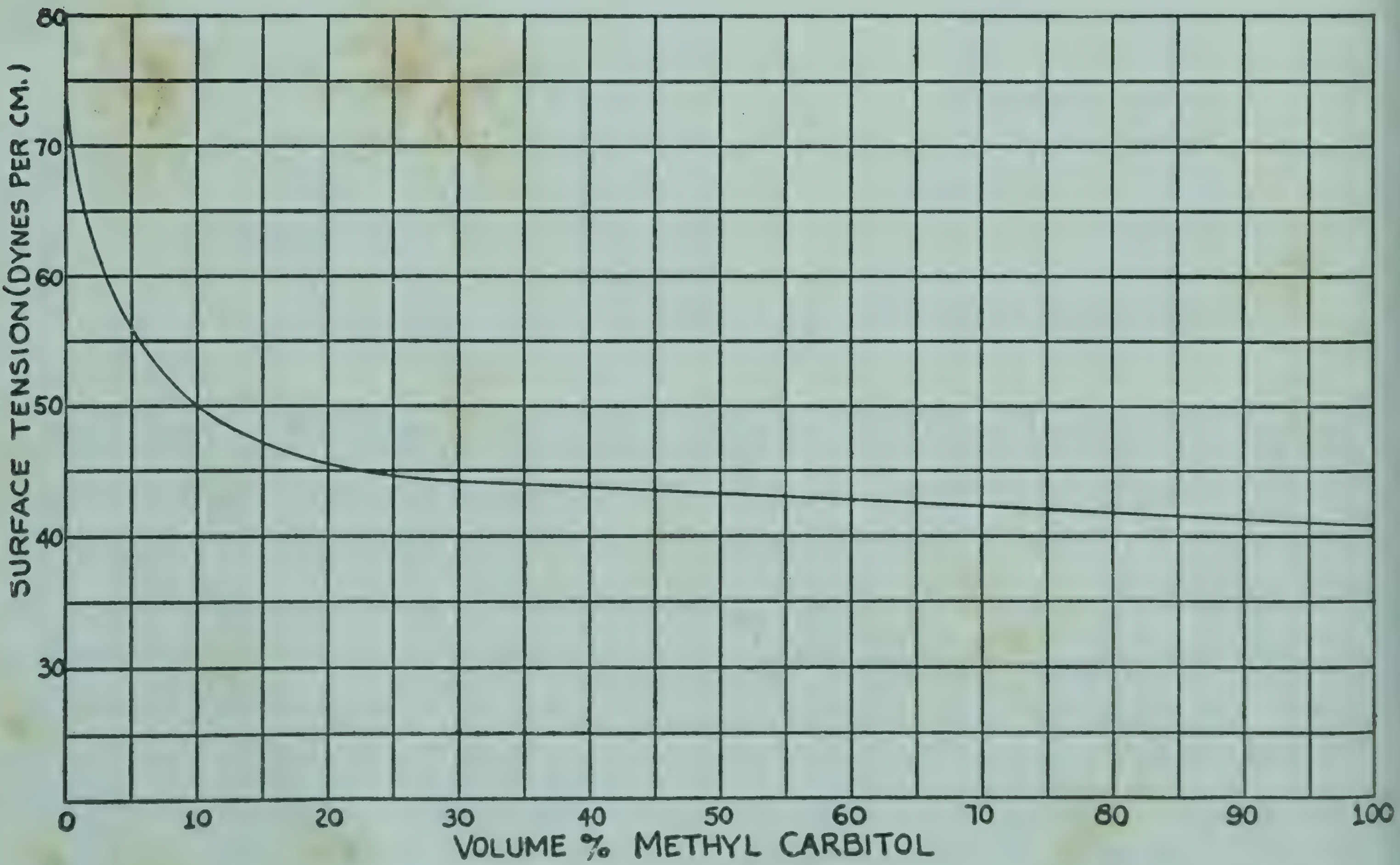


FIGURE 15.39. Surface Tension of Methyl "Carbitol"-Water Mixtures at 25°C.[2]

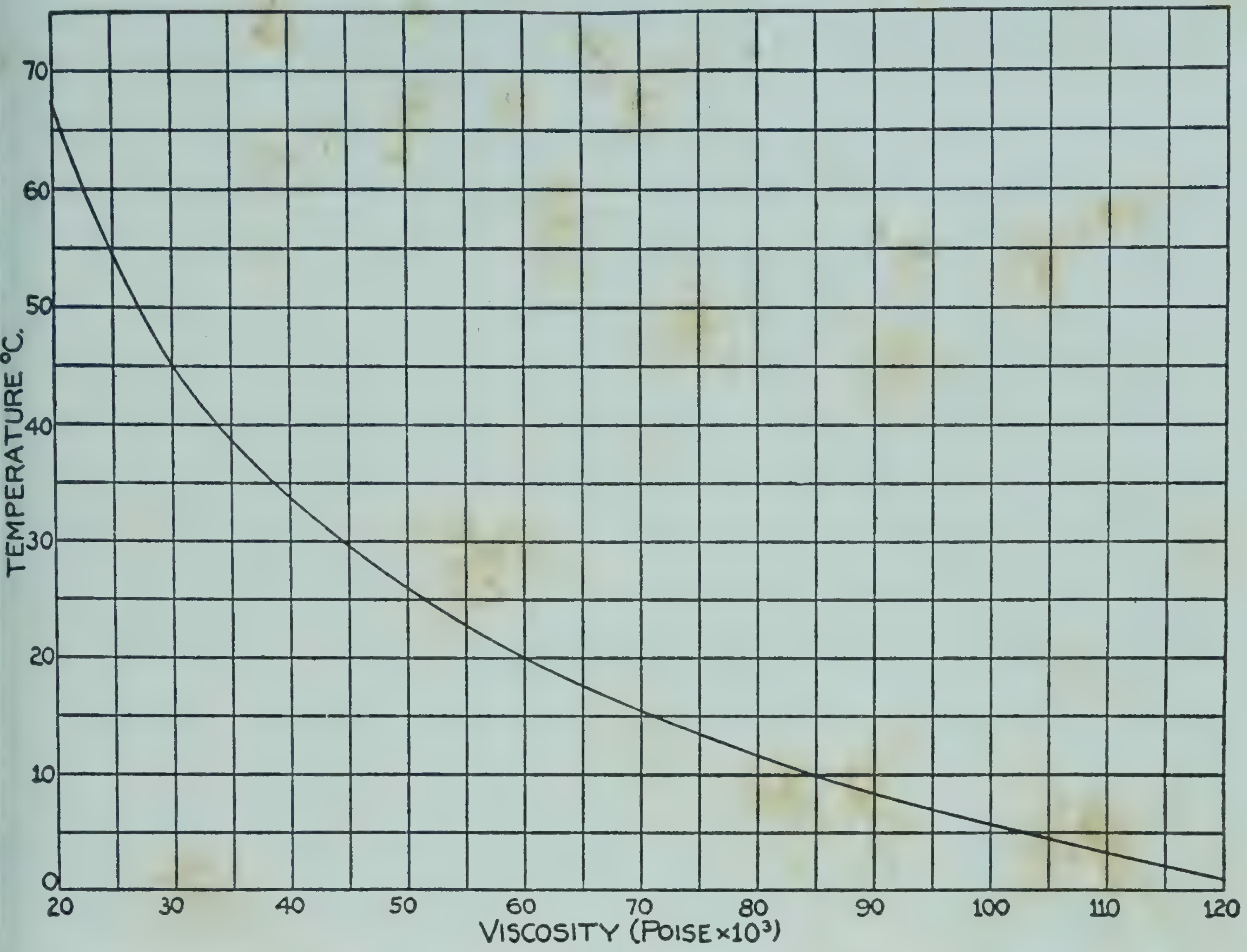


FIGURE 15.40. Viscosity of Methyl "Carbitol" at Various Temperatures.[2]

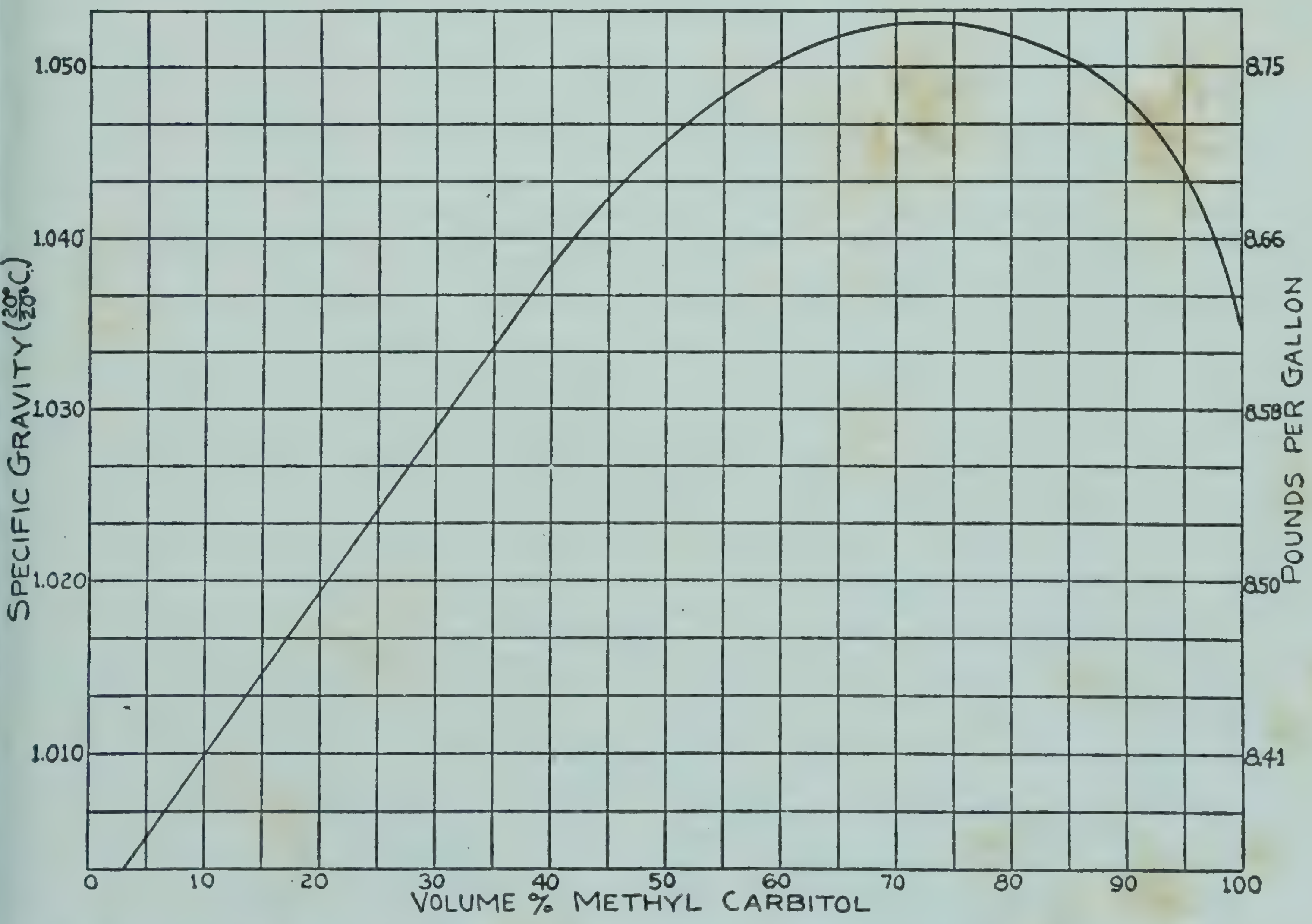


FIGURE 15.41. Specific Gravity and Weight per Gallon of Methyl "Carbitol"-Water Mixtures.[2]

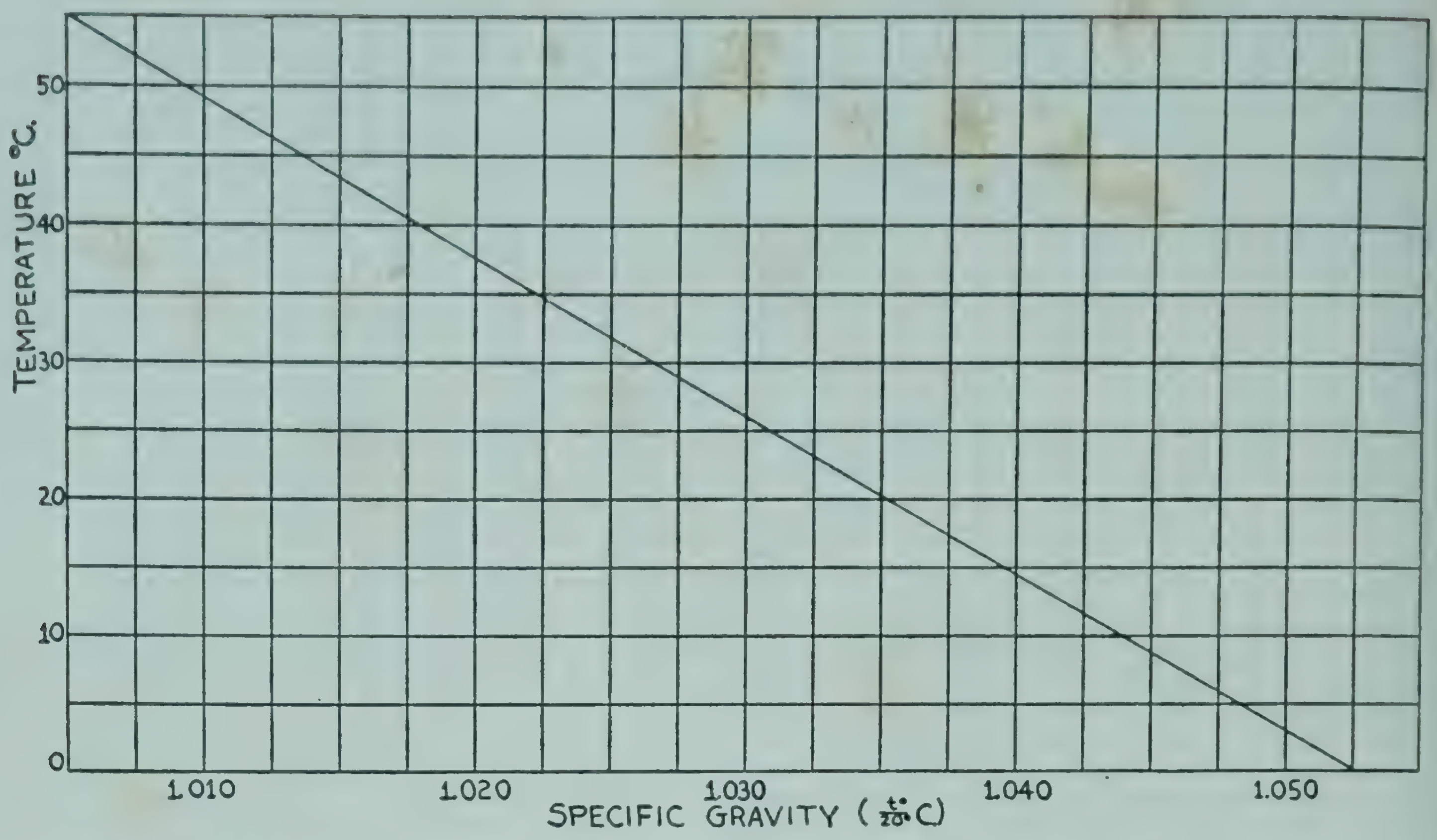


FIGURE 15.42. Specific Gravity and Weight per Gallon of Methyl "Carbitol" at Various Temperatures.[2]

glass manufacture, and in dyeing and printing mixtures, textile soaps in non-aqueous wood stains, in hydraulic brake fluids and manufacture of resin plasticizers.

Physical Properties

Molecular weight	134.11
Boiling point	201.9°C
Freezing point	<-76°C
Specific gravity	0.9902 at $\frac{20°C}{20°C}$
Weight per gallon	8.24 lb. (20°C)
Refractive index	1.4244 (26°C)
Surface tension	35.5 dynes/cm (25°C)
Viscosity	0.0385 poise (25°C)
Vapor pressure	0.13 mm Hg (20°C)
Specific heat	0.552 cal/g (20–25°C)
Heat of vaporization	96.3 cal/g
Flash point	99°C (210°F) (ASTM open cup)
Electrical conductivity	2.5×10^{-8} recip ohms (25°C)
Solubility in water	Complete
Dilution ratio	Toluene 1.65

Specifications

Specific gravity at 20/20°C	1.0240–1.0300
Distillation range	185°–205°C
Acidity (as acetic)	0.02% by wt max
Color (A.P.H.A.)	15 max

(*Text continued on page 666*)

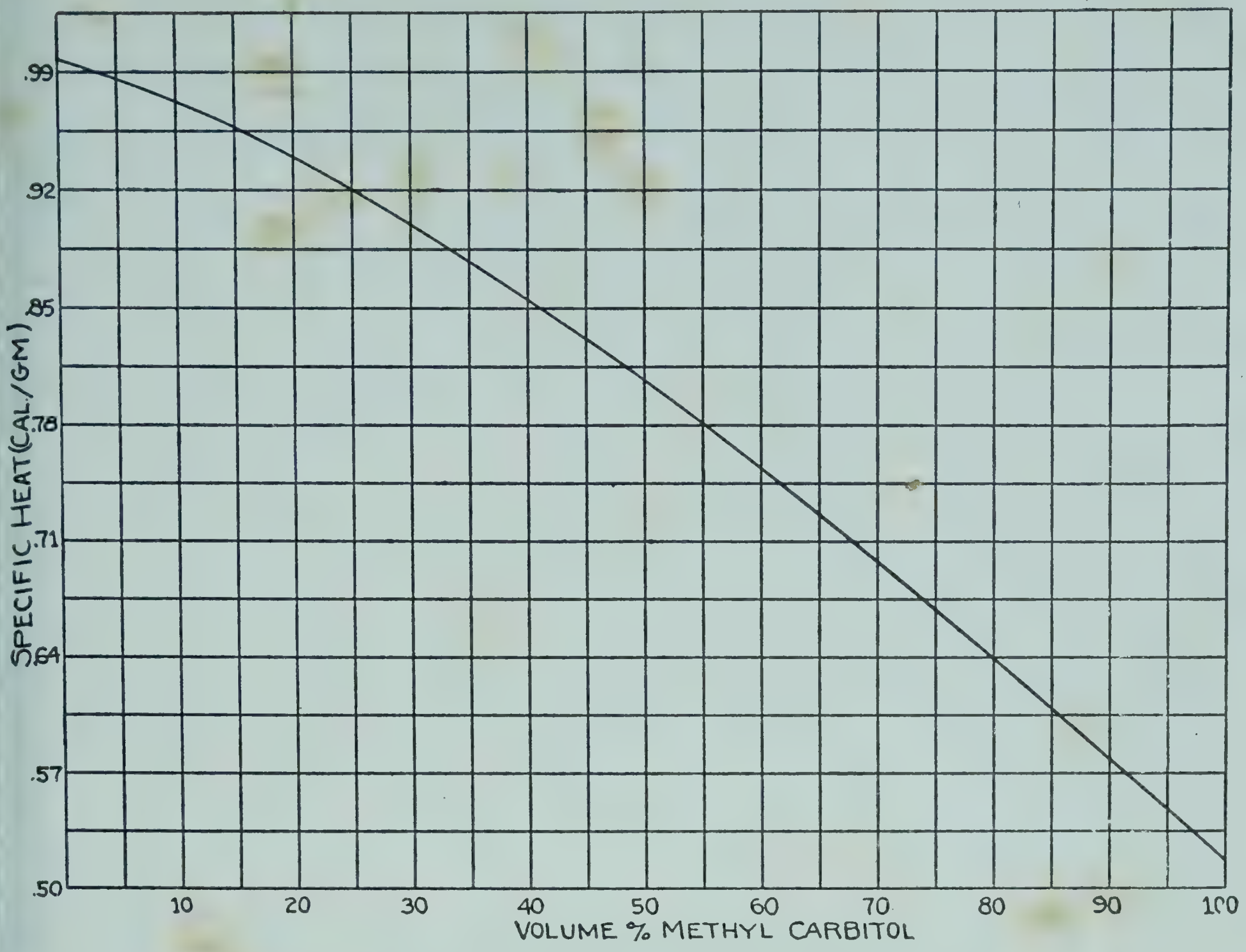


FIGURE 15.43. Specific Heat of Methyl "Carbitol"-Water Mixtures (20–25°C).[2]

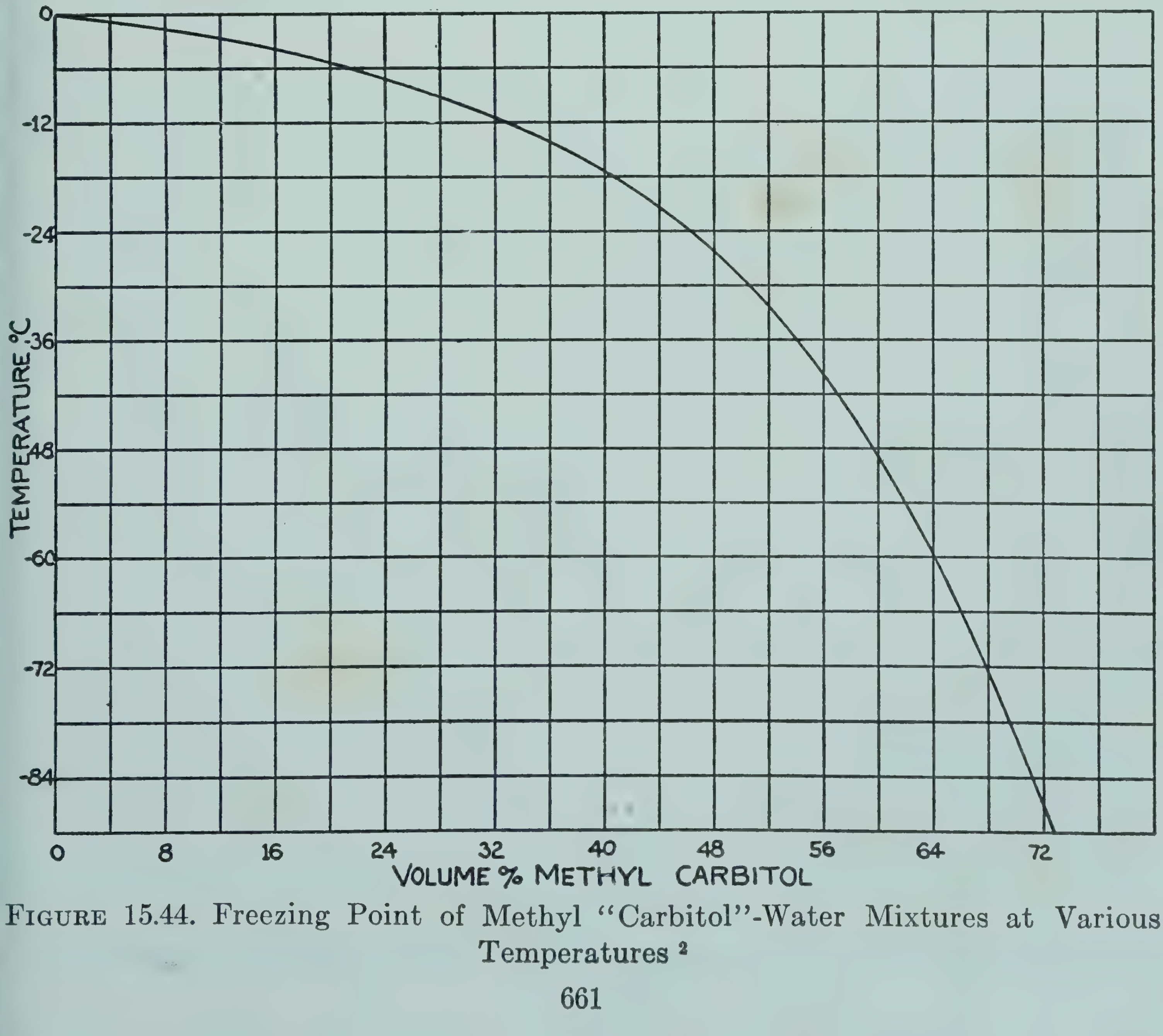


FIGURE 15.44. Freezing Point of Methyl "Carbitol"-Water Mixtures at Various Temperatures [2]

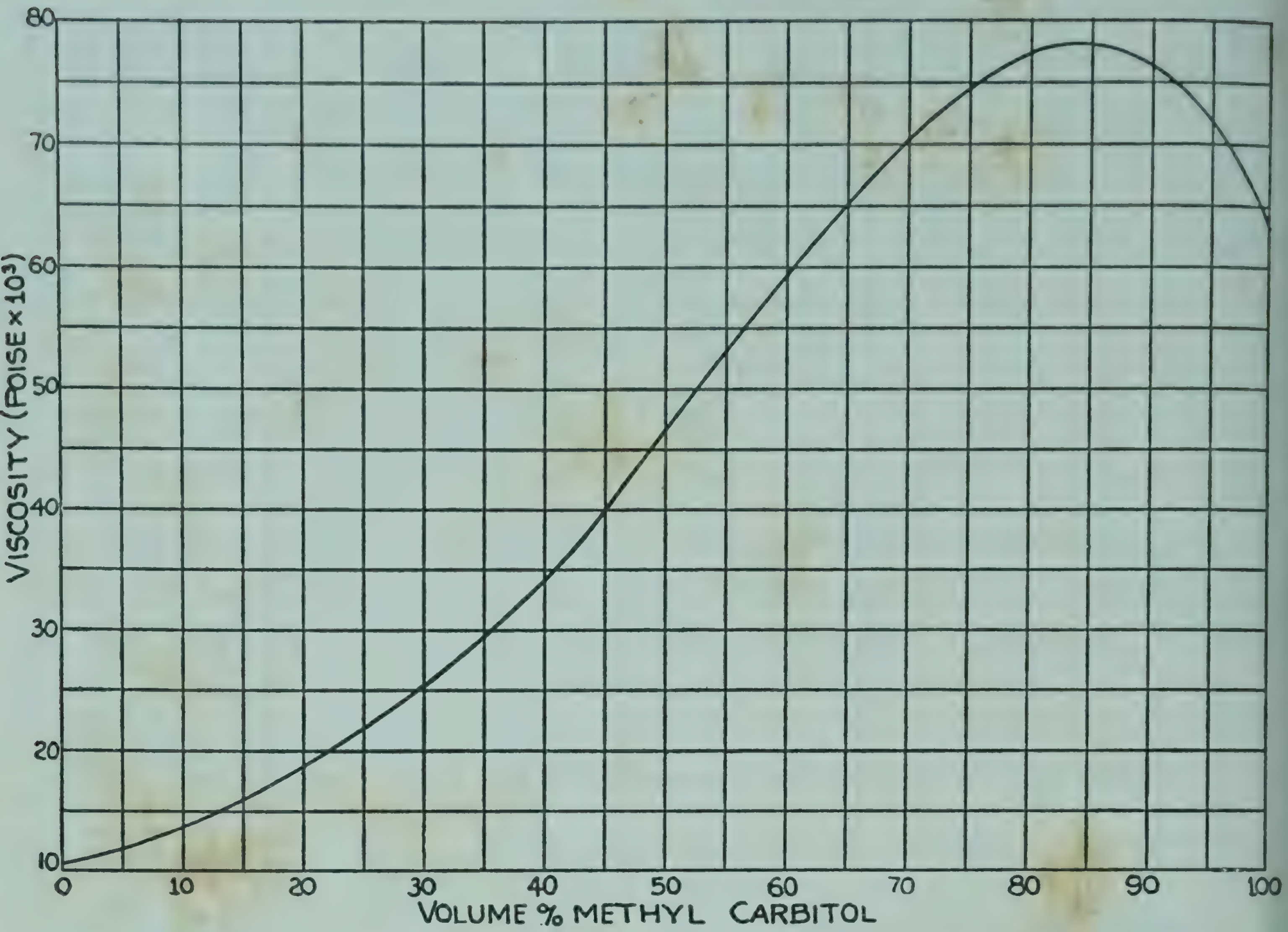


FIGURE 15.45. Viscosity of Methyl "Carbitol"-Water Mixtures at 20°C.[2]

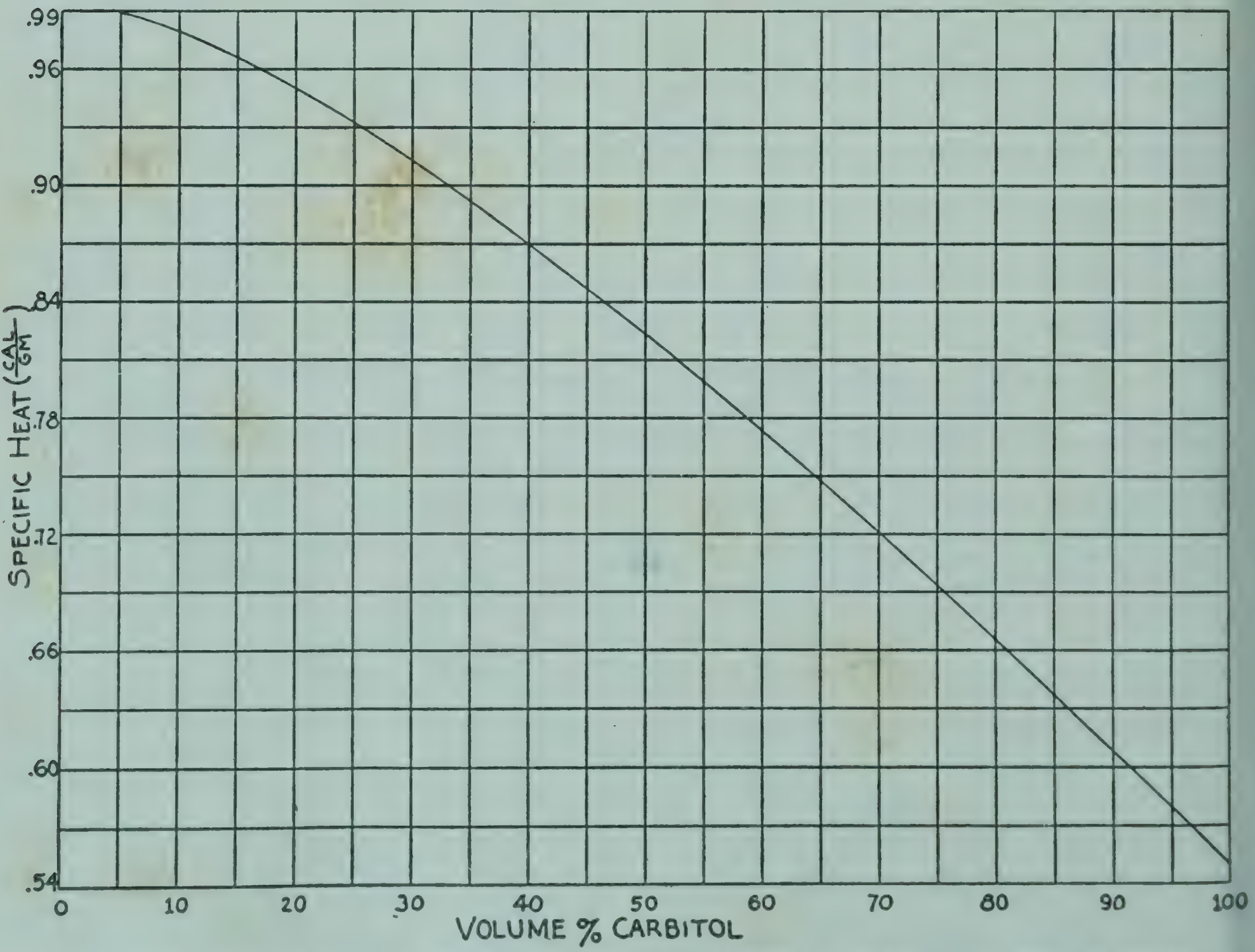


FIGURE 15.46. Specific Heat of "Carbitol"-Water Mixtures (20–25°C).[2]

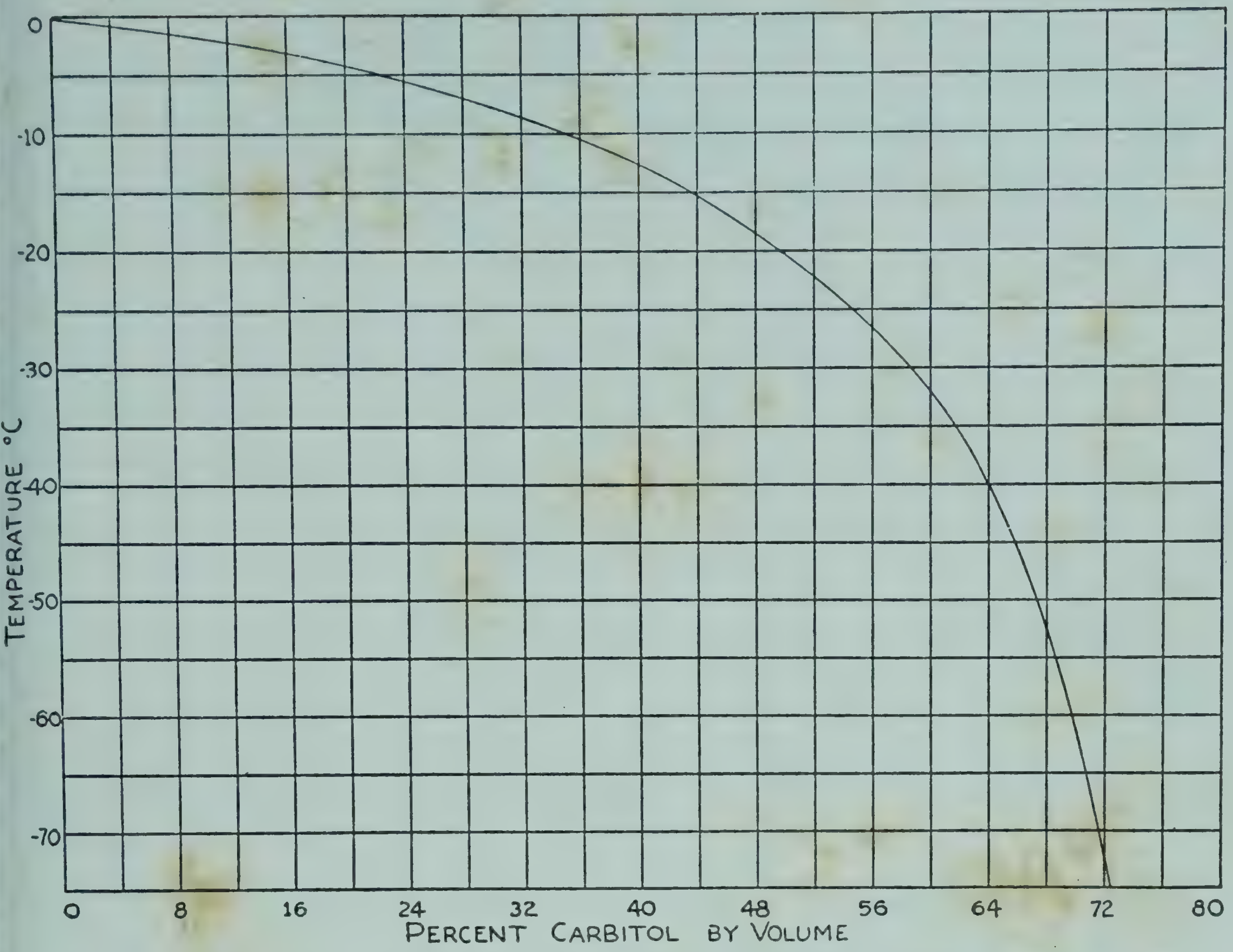


FIGURE 15.47. Approximate Freezing Point of "Carbitol"-Water Mixtures.[2]

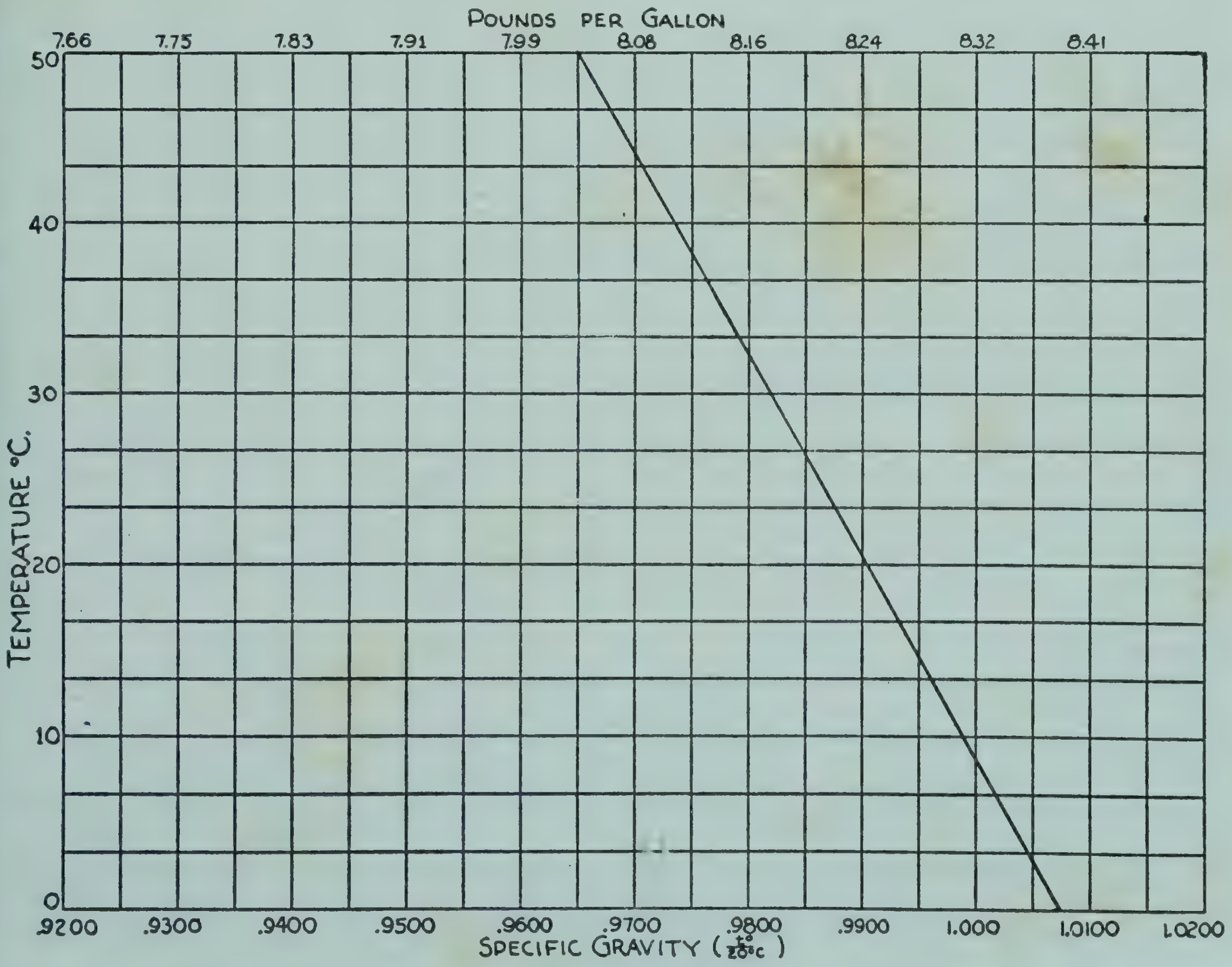


FIGURE 15.48. Specific Gravity and Weight per Gallon of "Carbitol" at Various Temperatures[3]

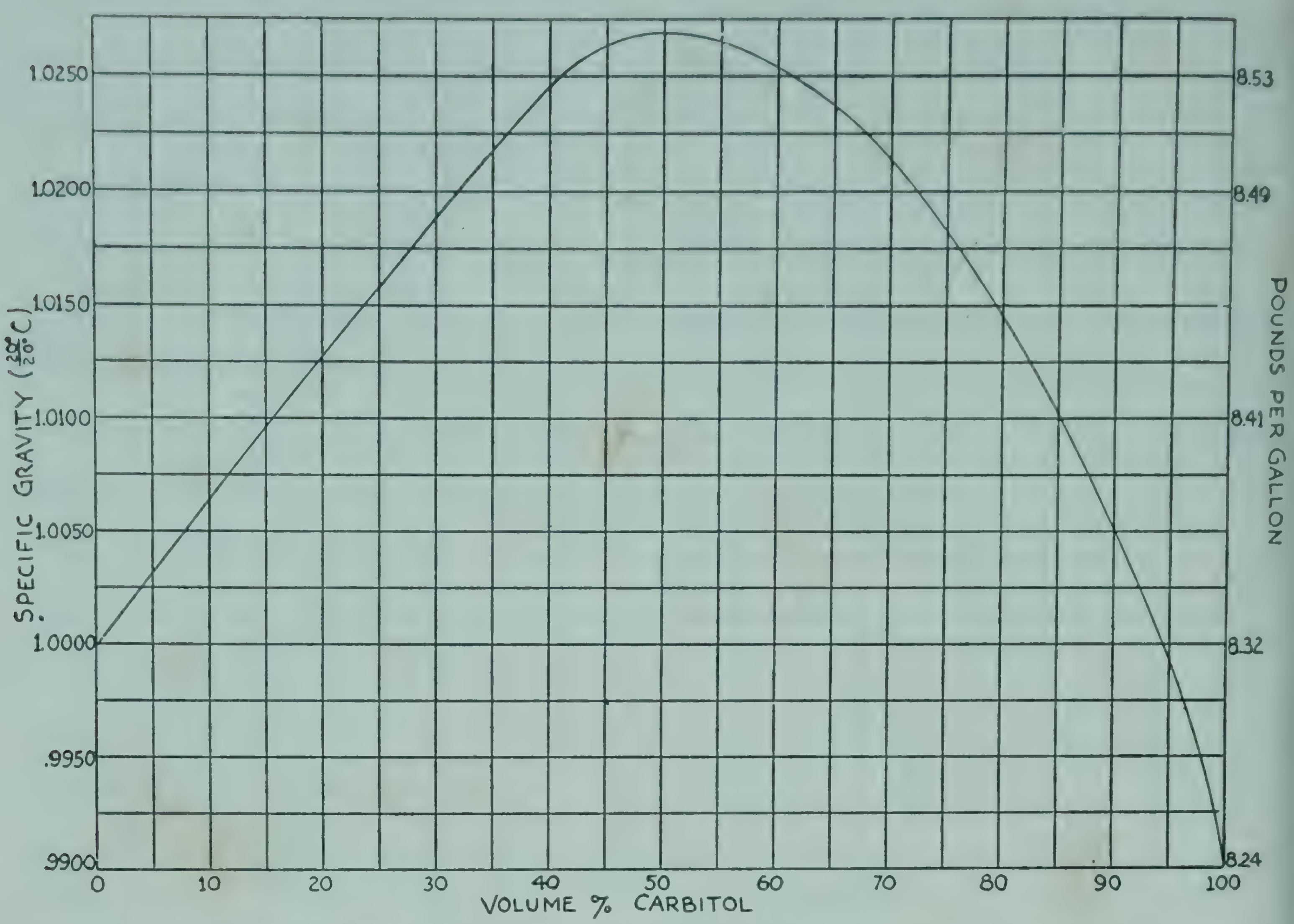


Figure 15.49. Specific Gravity and Weight per Gallon of "Carbitol"-Water Mixtures.[2]

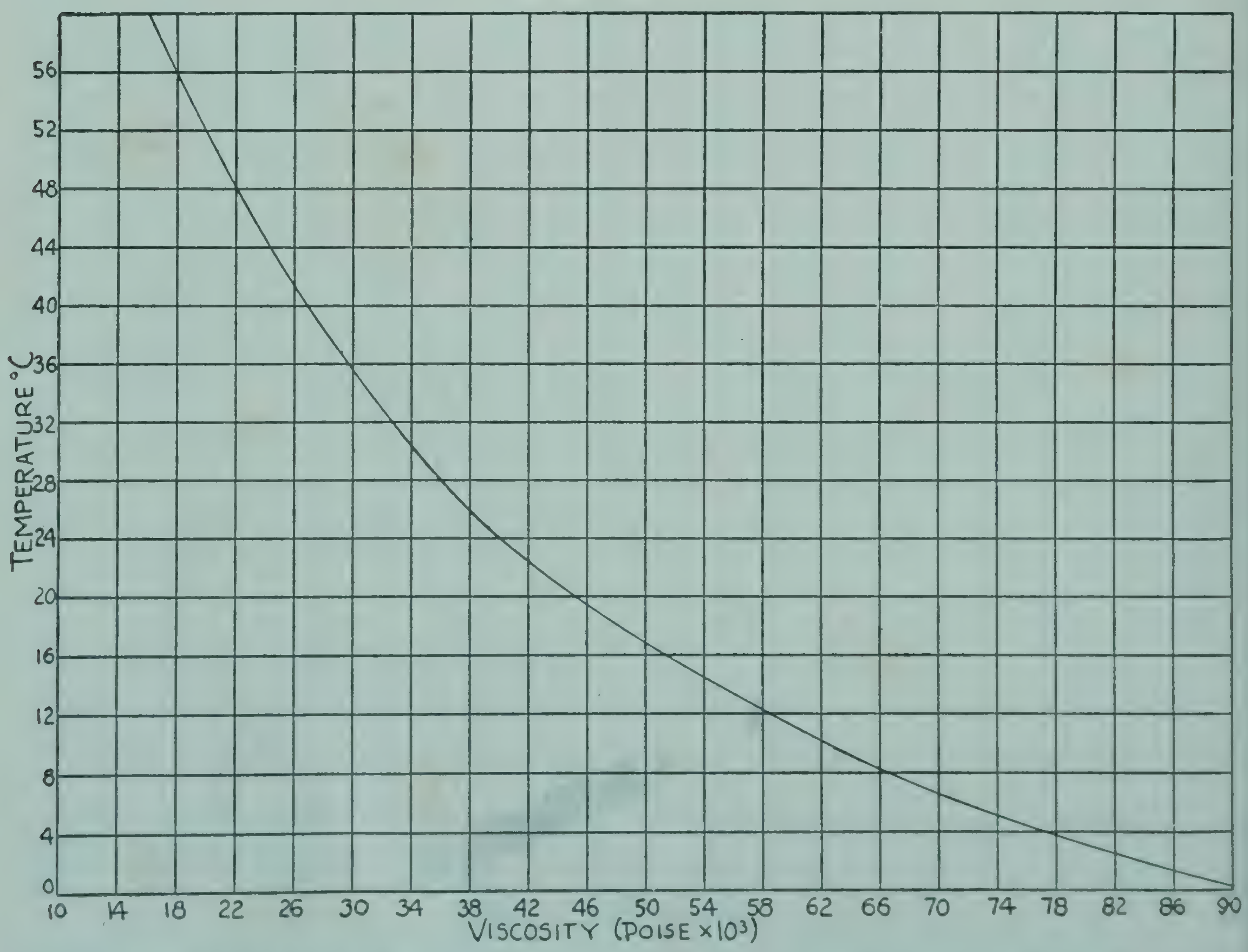


Figure 15.50. Viscosity of "Carbitol" at Various Temperatures.[2]

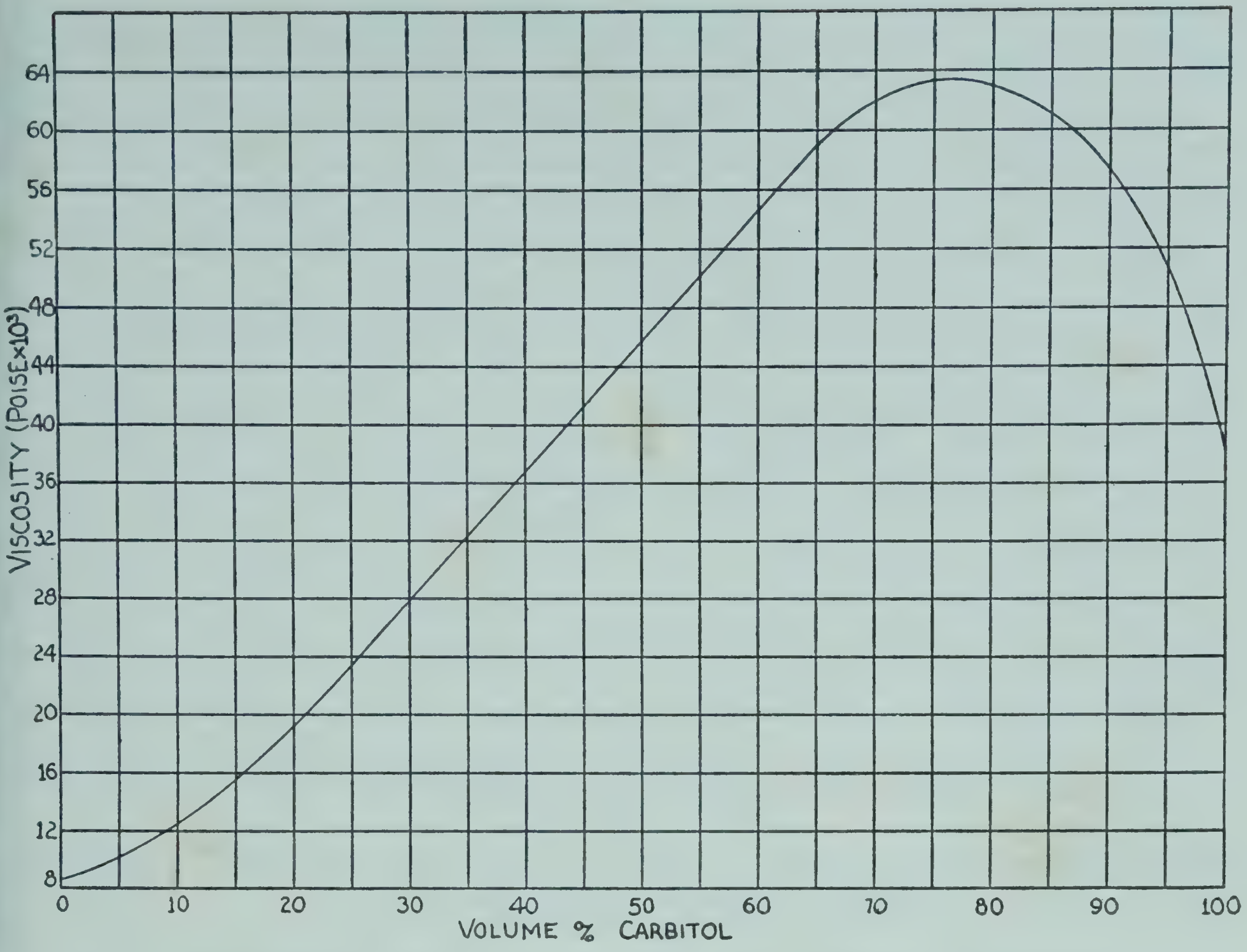


FIGURE 15.51. Viscosity of "Carbitol"-Water Mixtures at 25°C.[2]

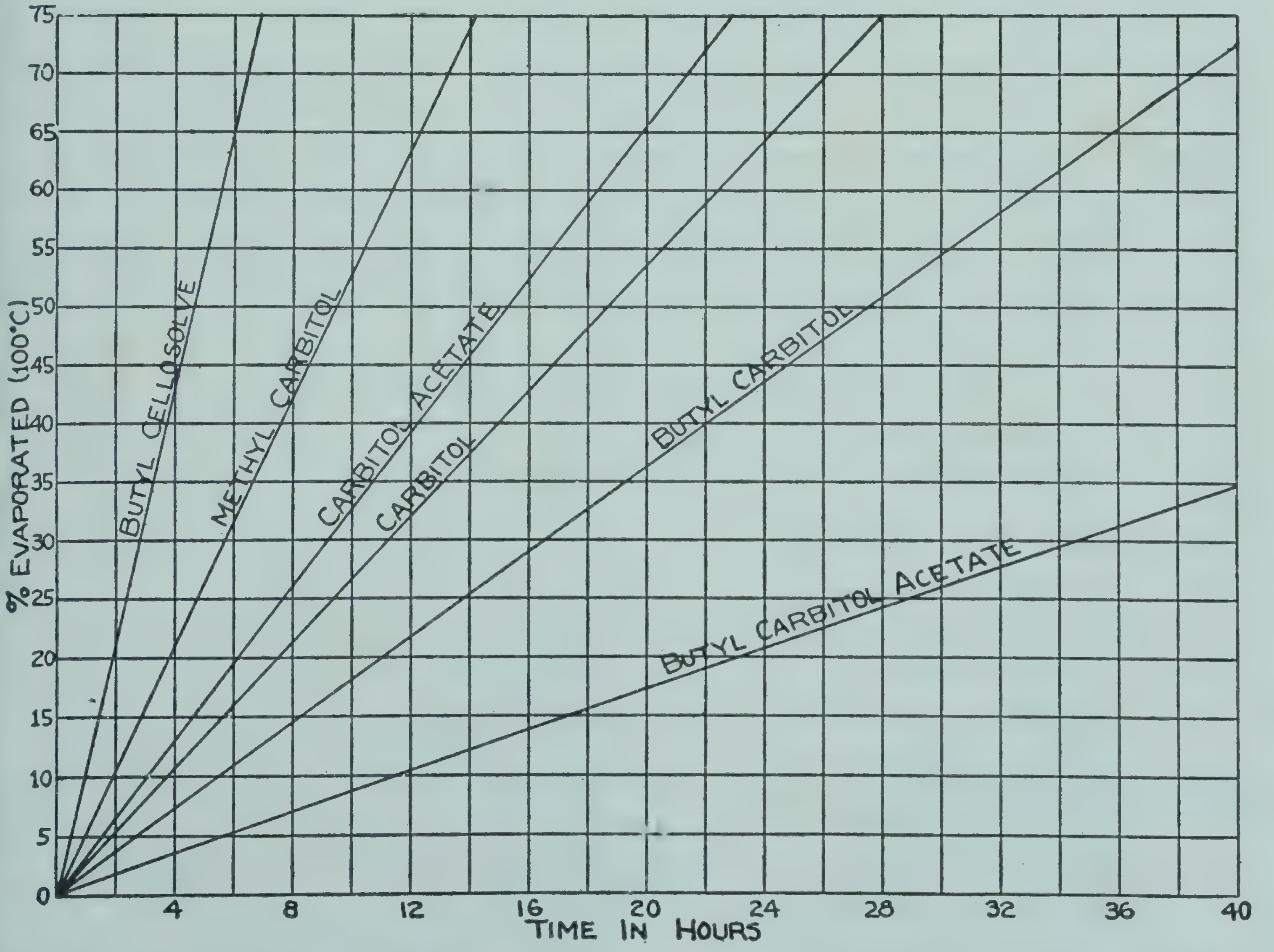


FIGURE 15.52. Evaporation Rate of Various Solvents at Room Temperature.[2]

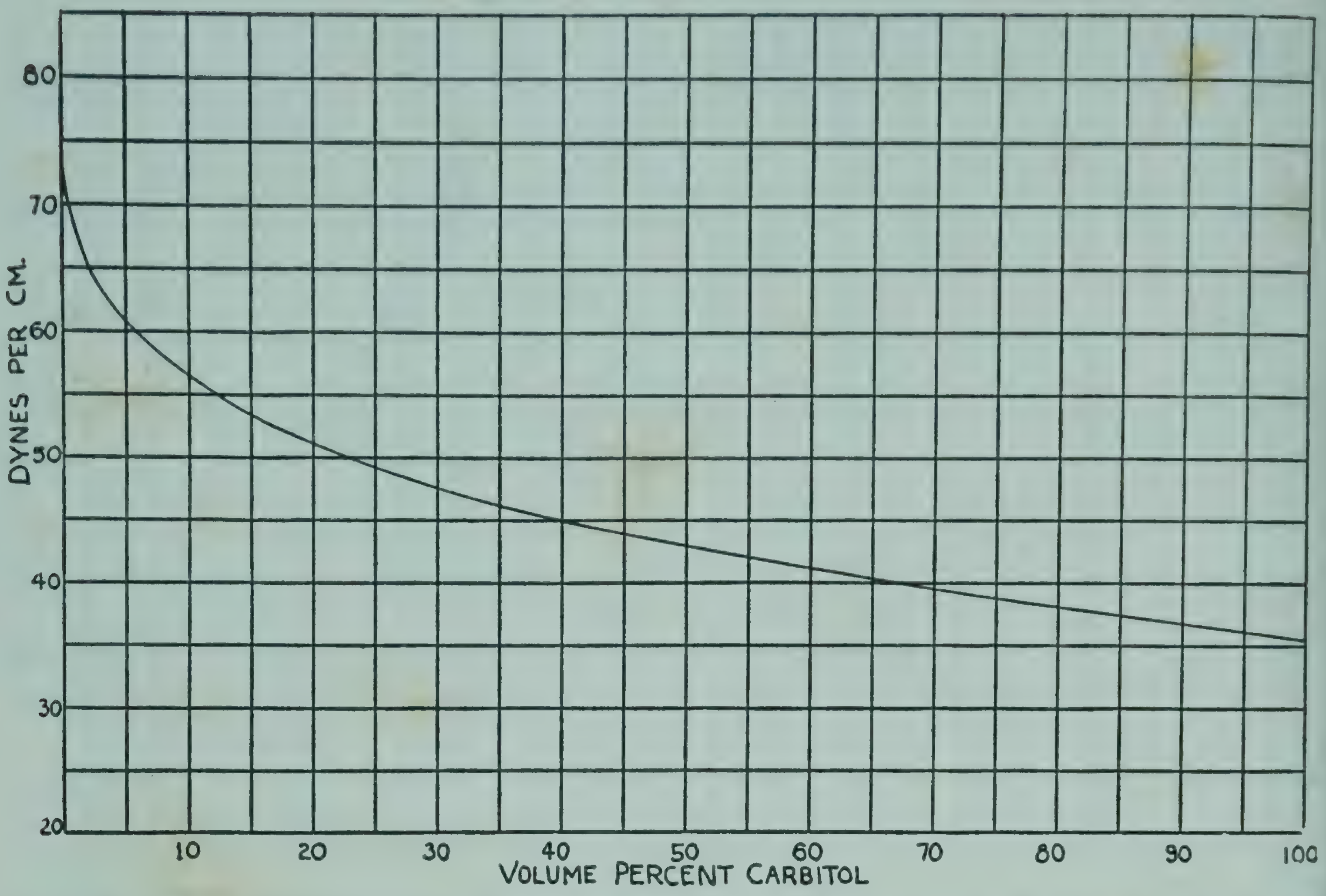


FIGURE 15.53. Surface Tension of "Carbitol"-Water Mixtures at 25°C[2] (du Noüy Apparatus—Water = 73 dynes/sq. cm.).

Diethylene Glycol Monobutyl Ether (Butyl "Carbitol") ($C_7H_9OCH_2CH_2OCH_2CH_2OH$). Diethylene Glycol Monobutyl Ether is a colorless high boiling liquid miscible in all proportions with water and many organic solvents. As it is an ether-alcohol type compound it possesses solvent action for many substances such as oils, dyes, gums, and natural and synthetic resins. Butyl "Carbitol" is used as a high-boiling solvent in nitrocellulose lacquers and other synthetic coatings, baking lacquers, flash-dry printing inks, and dye baths. It is useful as a mutual solvent in textile soap compositions.

Physical Properties

Molecular weight	162.14
Boiling point	231.2°C
Specific gravity	0.9553 at $\frac{20°C}{20°C}$
Weight per gallon	7.95 lb (20°C)
Refractive index	1.4290 (27°C)
Surface tension	33.6 dynes/cm (25°C)
Viscosity	0.0525 poise (20°C)
Vapor pressure	0.06 mm Hg (20°C)
Specific heat	0.546 cal/g (20–25°C)
Heat of vaporization	61.9 cal/g
Flash point	110°C. (230°F) (ASTM open cup)
Solubility in water	Complete
Coefficient of expansion	0.00087 (per°C) to 20°C

(Text continued on page 671)

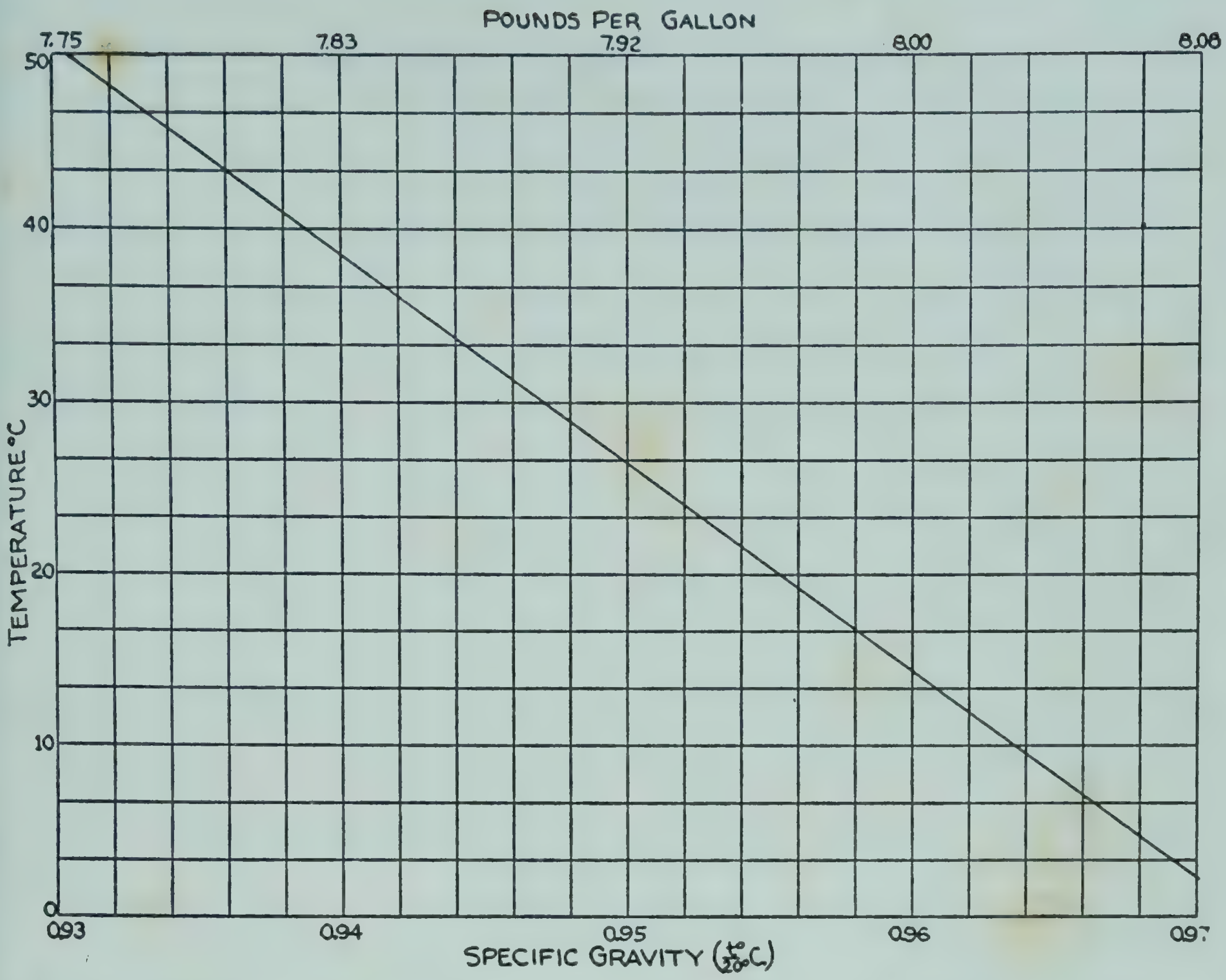


FIGURE 15.54. Specific Gravity and Weight per Gallon of Butyl "Carbitol" at Various Temperatures.[2]

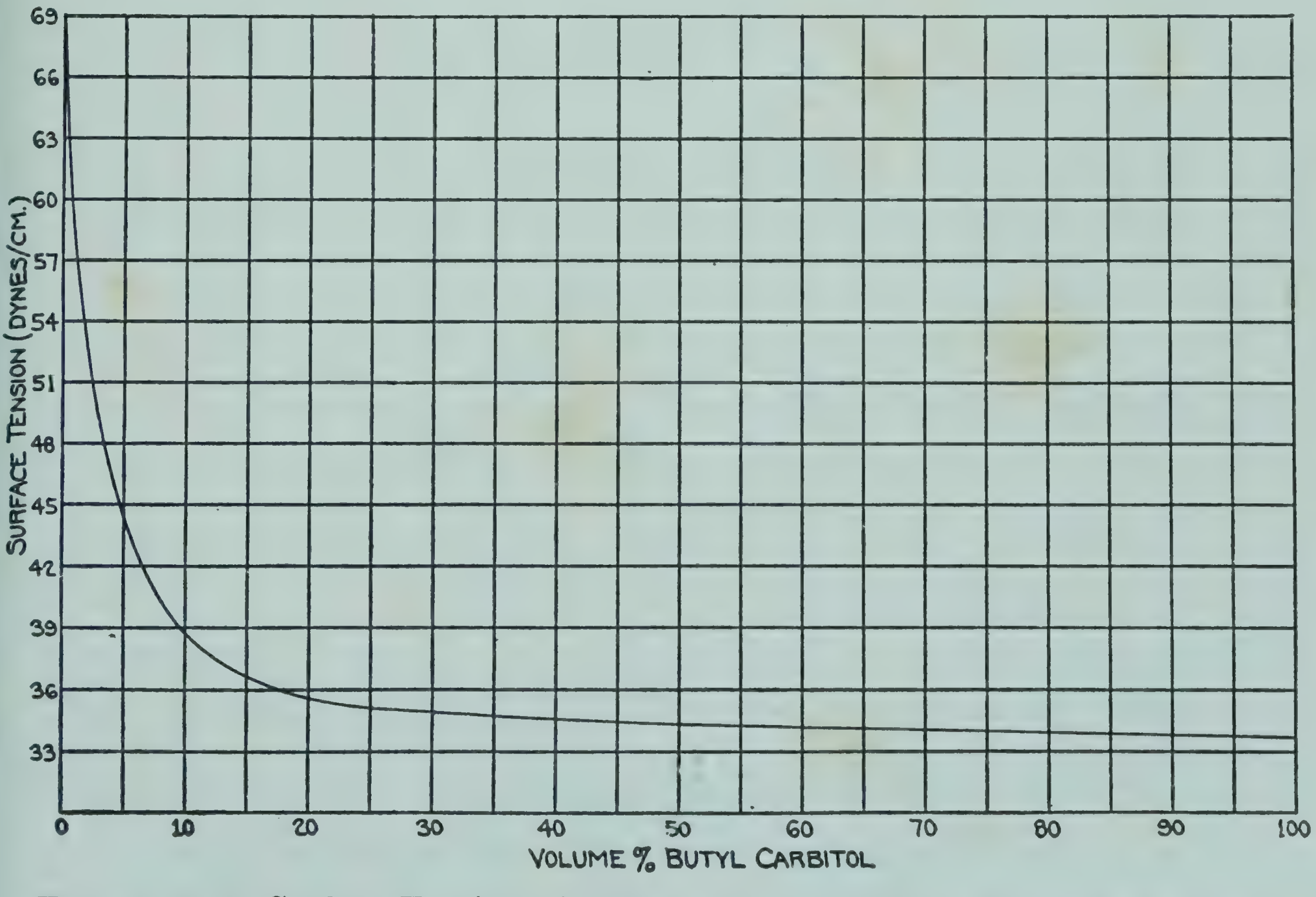


FIGURE 15.55. Surface Tension of Butyl "Carbitol"-Water Mixtures at 25°C.[2]

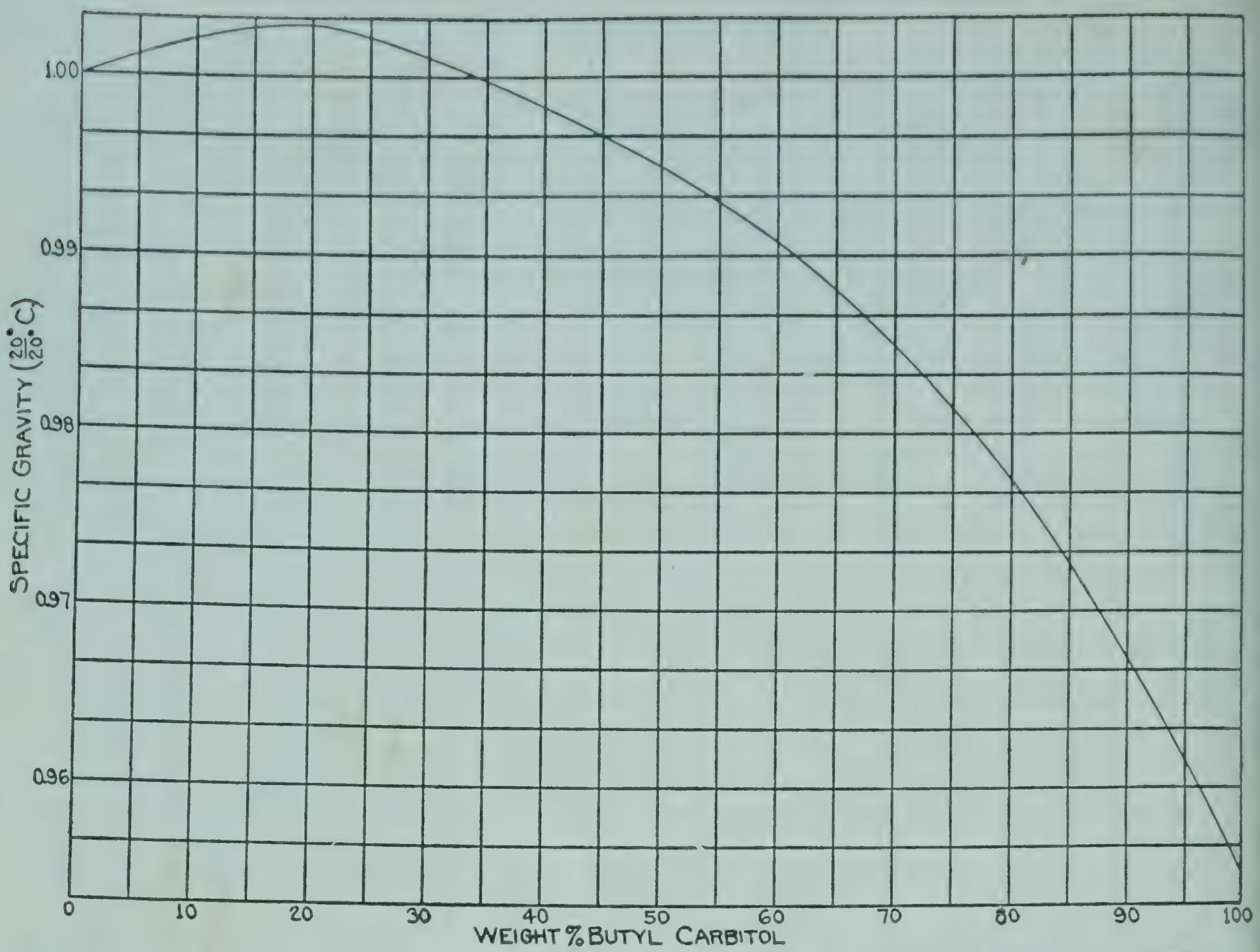


FIGURE 15.56. Specific Gravity and Weight per Gallon of Butyl "Carbitol"-Water Mixtures.[2]

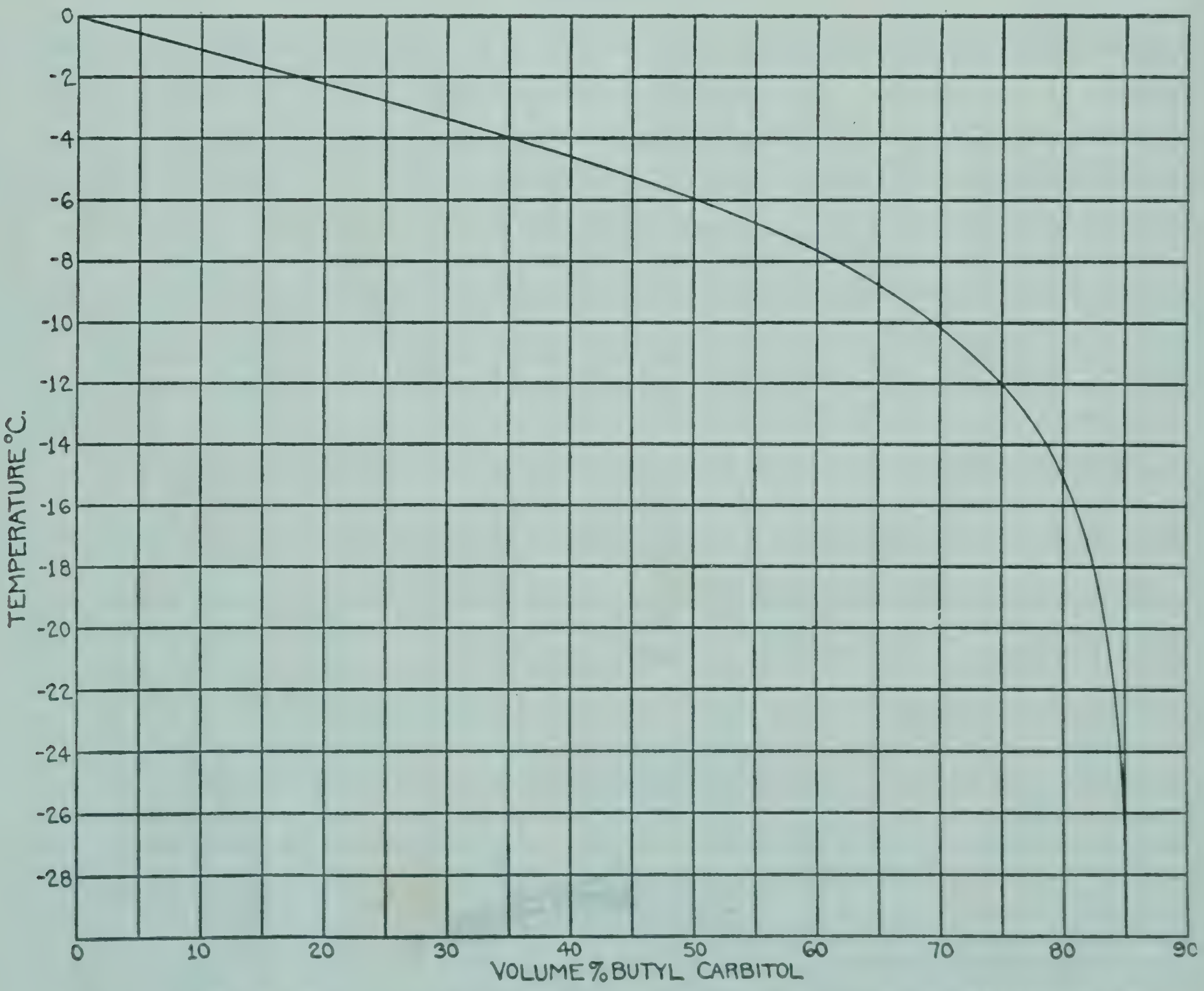


FIGURE 15.57. Freezing Point of Butyl "Carbitol"-Water Mixtures.[2]

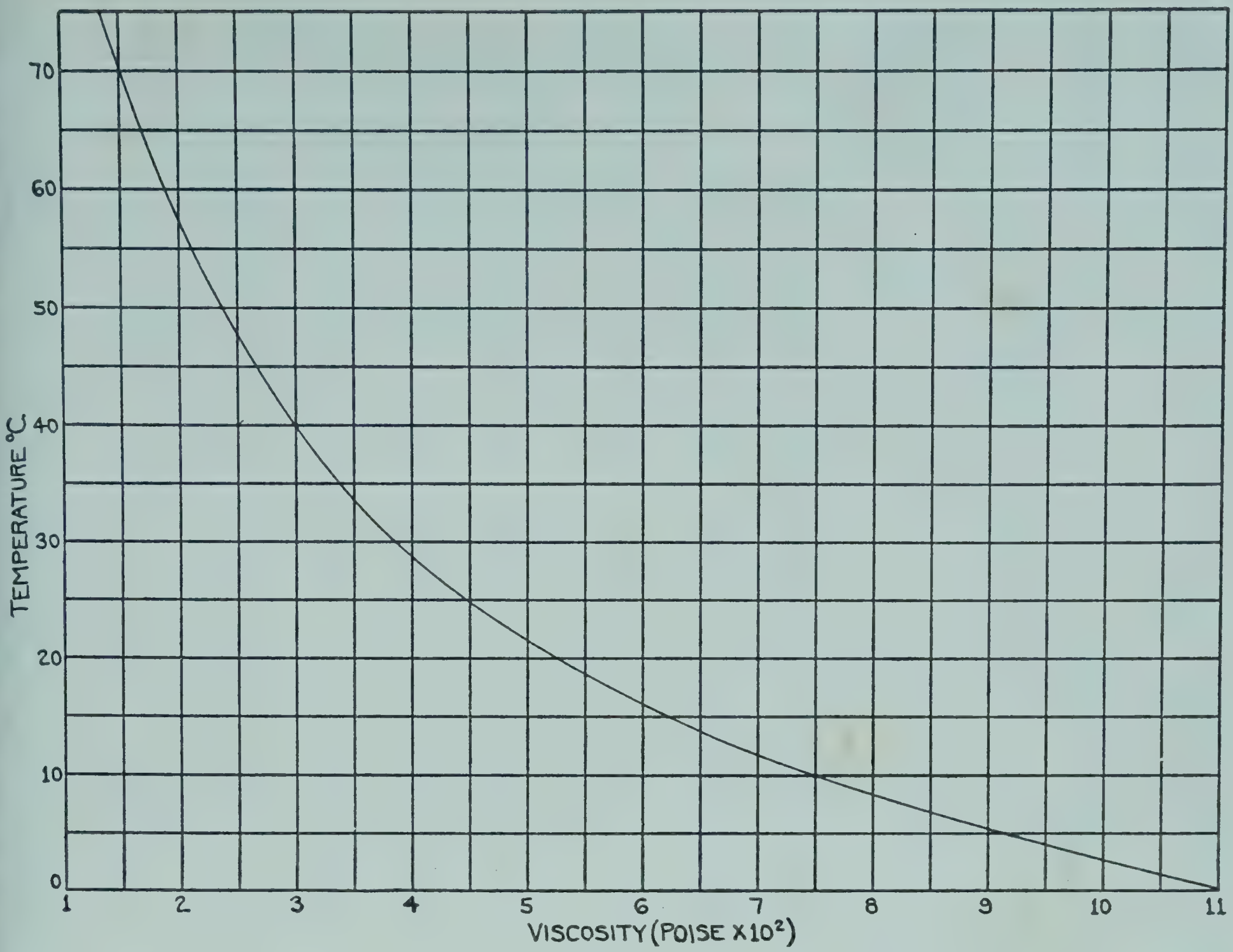


FIGURE 15.58. Viscosity of Butyl "Carbitol" at Various Temperatures.[2]

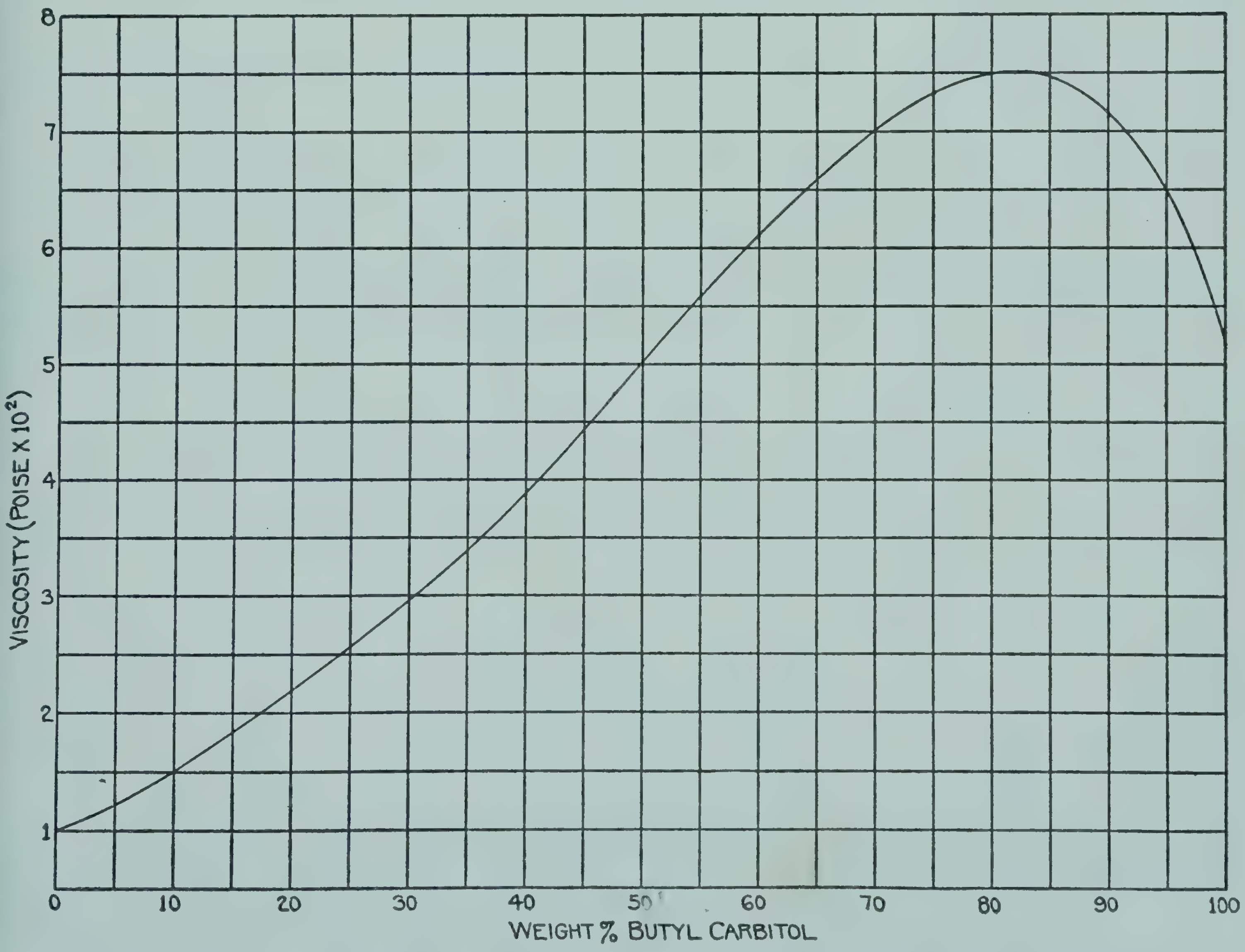


FIGURE 15.59. Viscosity of Butyl "Carbitol"-Water Mixtures at 20°C.[2]

Physical Properties of Dowanols[5] (Reference Data for Development Purposes on the Aliphatic Dowanols)

Dowanol No.	Compound	Formula	Mol. Wt.	Boiling Range of Sample, °C at 760 mm Hg		Boiling Point of Pure Compound, °C			Vapor Pressure at 25°C mm Hg	Density 25°C lb./gal.	Specific Gravity T/4°C		Viscosity cps		Freezing Point* °C	Refractive Index 25°C	Flash Point °C	Fire Point °C	Solubilities	
				5%	95%	760 mm	10 mm	0.1 mm			25°C	75°C	25°C	75°C					gm./100 gm. water at 25°C	Organic solvents
33B	Propylene Glycol, Methyl Ether	$C_4H_{10}O_2$	90.1	117	121	119	21	−37	13	7.63	.916	.866	1.7	.65	−100 to −105	1.401	43	43	∞	†
34B	Propylene Glycol, Ethyl Ether	$C_5H_{12}O_2$	104.2	131	139	132	30	−29	7.2	7.42	.891	.841	1.9	.67	−95 to −100	1.405	55	55	∞	†
37B	Propylene Glycol, n-Butyl Ether	$C_7H_{16}O_2$	132.2	170	172	170	60	−6	1.2	7.29	.875	.829	2.9	.91	−90 to −95	1.415	74	74	6.0	†
50B	Dipropylene Glycol, Methyl Ether	$C_7H_{16}O_3$	148.2	187	192	189	74	6	0.44	7.91	.950	.903	3.5	1.1	−80 to −85	1.419	85	85	∞	†
51B	Dipropylene Glycol, Ethyl Ether	$C_8H_{18}O_3$	162.2	196	205	197	81	12	0.30	7.72	.927	.881	3.4	1.1	−70 to −75	1.419	90	90	∞	†
54B	Dipropylene Glycol, n-Butyl Ether	$C_{10}H_{22}O_3$	190.3	228	233	228	105	31	0.06	7.61	.914	.871	5.0	1.4	−70 to −75	1.425	116	116	4.3	†
62B	Tripropylene Glycol, Methyl Ether	$C_{10}H_{22}O_4$	206.3	241	247	242	116	39	0.03	8.00	.961	.917	5.5	1.6	−60 to −65	1.427	127	127	∞	†
63B	Tripropylene Glycol, Ethyl Ether	$C_{11}H_{24}O_4$	220.3			247	121	44	0.02	7.90	.947	.903	6.0	1.6	−55 to −60	1.427	134	134	∞	†
66B	Tripropylene Glycol, n-Butyl Ether	$C_{13}H_{28}O_4$	248.4			277	145	64	0.004	7.75	.929	.886	6.9	1.8	−65 to −70	1.430	140	152	1.5	†

* These Dowanols form a glass at the temperature indicated.

† These Dowanols are completely miscible at 25°C. with: Acetone, Benzene, Carbon Tetrachloride, Ethanol, Ether, Methanol, Monochlorobenzene, Petroleum Ether, VMP Naphtha.

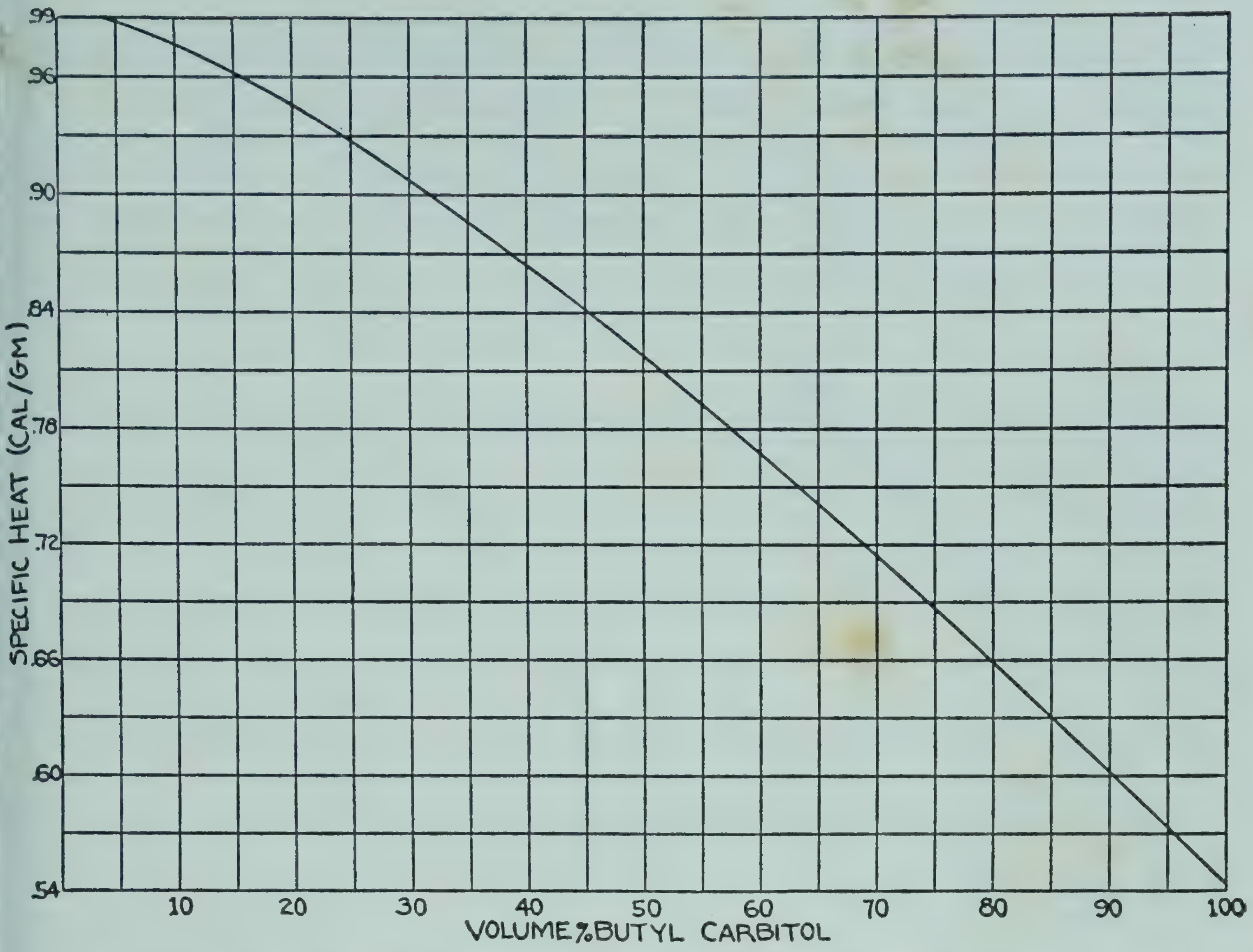
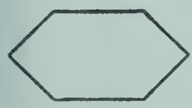


FIGURE 15.60. Specific Heat of Butyl "Carbitol"-Water Mixtures (20–25°C).[2]

Dowanol 2[5] (Propylene glycol, phenyl ether) (1-Phenoxy-2-Propanol) $O \cdot CH_2 \cdot CHOH \cdot CH_3C_9H_{12}O_2 = 152.2$) This is a clear, colorless liquid with a slight pleasant odor.

Boiling range at 760 mm Hg, 5–95%	241–267°C
Specific gravity at 25/25°C	1.061
Freezing point	13°C
Refractive index at 25°C	1.520
Flash point	113°C
Fire point	121°C
Viscosity at 25°C, centipoises	24
60°C, centipoises	4

ACETALS

Acetals are the polyethers of polyvalent alcohols made by condensing aldehydes or ketones with polyhydric alcohols.

Diethyl Acetal, (α,α-Diethoxyethane, diethylaldehyde (ethylidene diethyl ether acetal acetaldehyde) [$CH_3CH(OC_2H_5)_2$]. Diethyl acetal is a

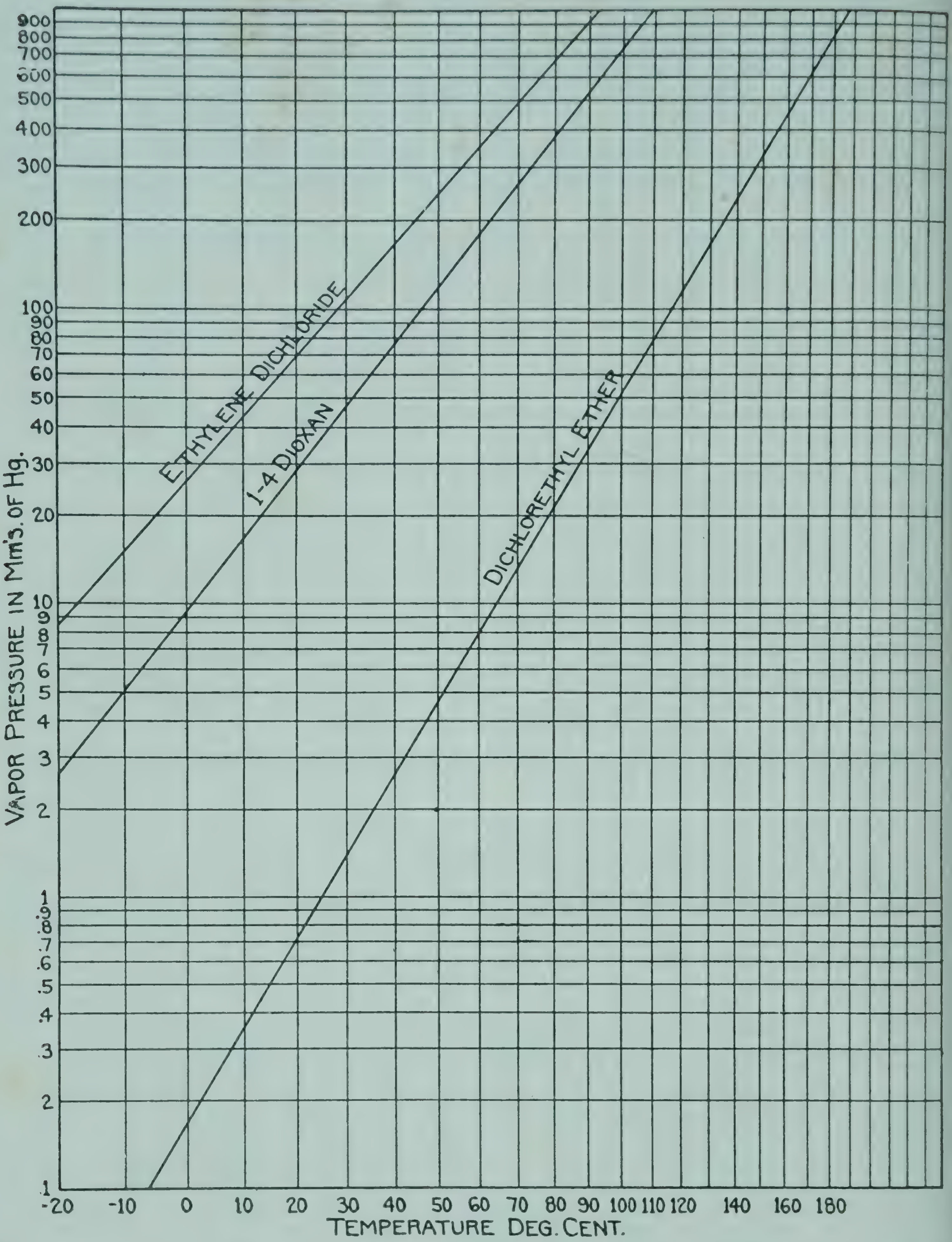
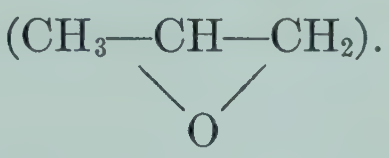


FIGURE 15.61. Vapor Pressure of Some Organic Solvents at Various Temperatures.[2]

stable water-white, mobile liquid with a pleasant odor. It is completely miscible with ethyl alcohol and ethyl ether and its solvent properties resemble those of a mixture of these two solvents. Dilute acids hydrolize it to acetaldehyde and ethyl alcohol.

Boiling point	103.6°C
Distillation range	97–112°C
Constant boiling mixture	
Diethyl acetal	34.5% b.p. 78.2°C
ethyl alcohol	65.5%
Metal, chlorine and sulfates	None
Purity	97% minimum
Specific gravity at 20°C	0.826–0.830
Weight per gal at 20°C	6.89 lbs

MISCELLANEOUS ETHERS

1, 2-Propylene Oxide  $(CH_3—CH—CH_2)$ with O bridging CH and CH_2. 1,2-Propylene oxide is a colorless, volatile liquid miscible with most organic solvents and very soluble in water. It is solvent for such natural and synthetic resins as shellac, Kauri, dammar, rosin, rosin ester, and vinyl resins. It will also dissolve cellulose esters, oils, hydrocarbons, and a large number of other products. This solvent is a low-boiler and finds use in nitrocellulose leather cements, fumigation of dried fruit and the manufacture of industrial solvents.

Acidity (as acetic)	0.05% by wt
Boiling point at 760 mm	34.1°C
Distillation range	30–40°C 95% distills within this range
Freezing point	−35°F
Specific gravity at 20/20°C	0.8313
Solubility in water at 20°C	41.0% by wt
Solubility of water in propylene oxide at 20°C	13.0% by wt
Vapor pressure at 20°C	395 mm Hg
Water content	1.0% by wt, max
Weight per gal at 20°C	6.92 lbs

1,4-Dioxane (1,4-Dioxan, 1,4-diethylene oxide, dioxyethylene ether, diethylene ether, diethylene dioxide) $(\underline{O—CH_2—CH_2—O—CH_2—CH_2})$.

1,4-Dioxane is a colorless, stable liquid with a faint, pleasant odor. Although it has been known as far back as 1863, it was not until 929 that it became commercially available. It is chemically a di-ether obtained by the loss of water from two molecules of ethylene glycol. It is completely soluble in water, as well as most organic solvents. It is freely soluble in mineral, vegetable, blown and heat-bodied oils, and oil-soluble dyes. Most waxes are more readily soluble in dioxane when heated and examples of these are beeswax, carnauba, montan, paraffin, gilsonite, and Japan wax. Water-

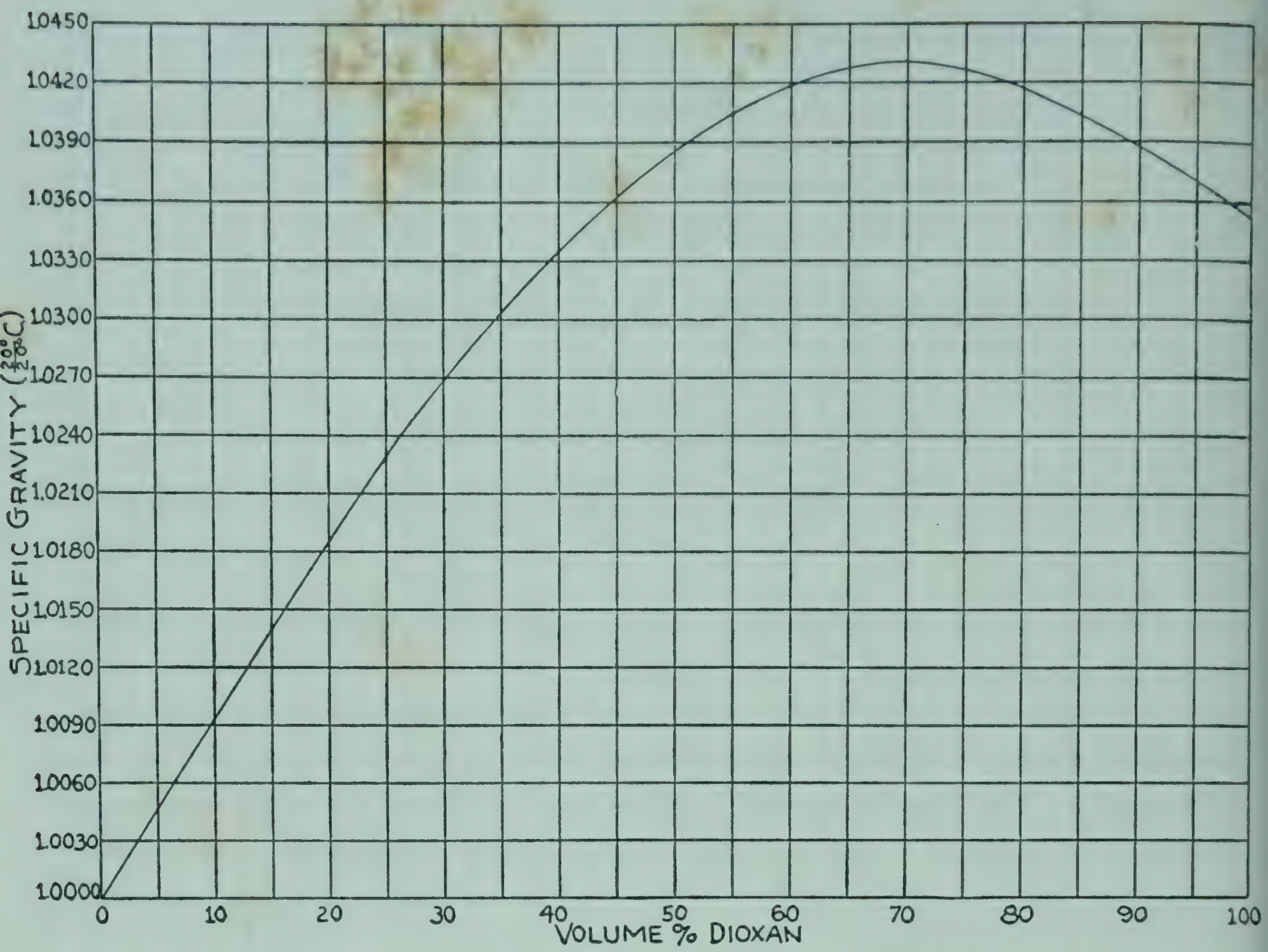


FIGURE 15.62. Specific Gravity of Water Solutions of 1,4-Dioxane.[2] Room Temperature.

soluble and spirit-soluble dyes are either partly or entirely insoluble in dioxane. Dioxane is a solvent for such natural resins as dewaxed dammar, elemi, guaiac, Kauri, manila, mastic, pontianac, rosin and shellac, and such synthetic resins as ester gum, cumar resins, alkyd, some types of vinyl resins, and cellulose ethers and esters. A mixture of dioxane and alcohol is a particularly good solvent for nitrocellulose.

Dioxane has been recommended as a solvent for the extraction of lignin and is widely used in laboratories in histologenol technics as a replacement for alcohol.[2] Dioxan has the tendency to form explosive peroxides when allowed to stand and these must be neutralized with an appropriate inhibitor.

Acidity (as acetic)	0.010% by wt, max
Boiling point 760 mm	101.3°C
Distillation range at 760 mm	95–103°C
Coefficient of expansion	0.001030 (per °C) to 20°C 0.001070 (per °C) to 55°C
Electrical conductivity at 25°C	2×10^{-8} recip. ohms
Flash point	65°F
Freezing point	11.7°C
Heat of combustion	581 kg cal/mol

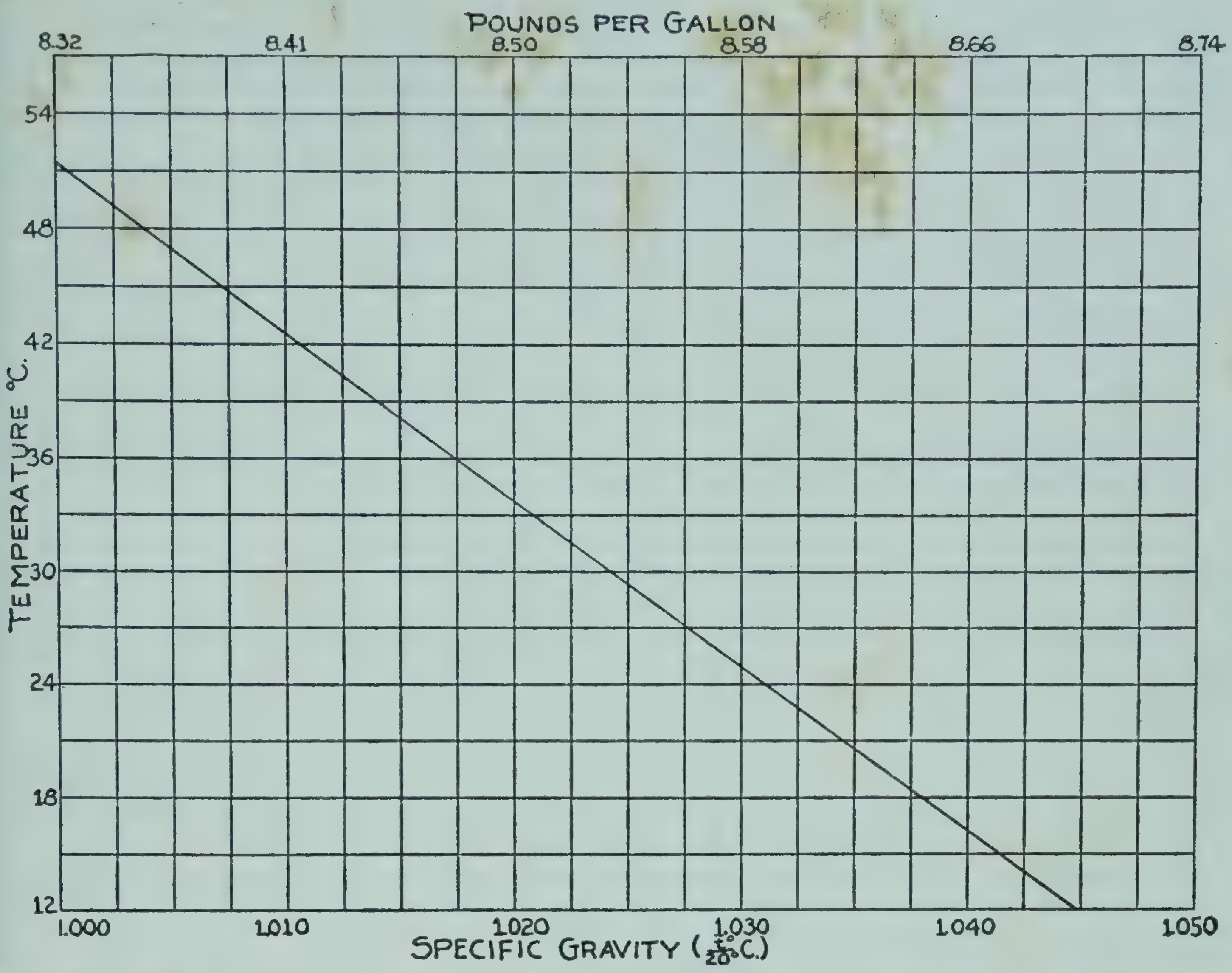
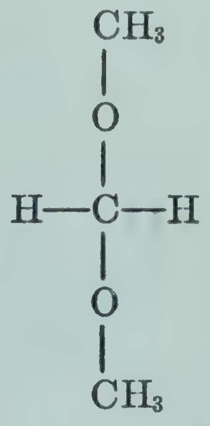


FIGURE 15.63. Specific Gravity and Weight per Gallon of 1,4-Dioxane at Various Temperatures.[2]

Heat of fusion	33.8 cal/g
Heat of vaporization	98.6 cal/g
Refractive index at 20°C	1.4221
Specific gravity at 20/20°C	1.0356 1.0353
Specific heat at 20°C	0.420 cal/g
Surface tension at 25°C	36.9 dynes/cm
Solubility in water at 20°C	Complete
Solubility of water in dioxane at 20°C	Complete
Viscosity at 25°C	0.0120 poise
Vapor pressure at 20°C	29.0 mm Hg
Water content at 20°C	Miscible without turbidity with 19 vol. 60° Be gasoline
Weight per gal at 20°C	8.61 lbs

Methylal:[6] (dimethoxy-methane)



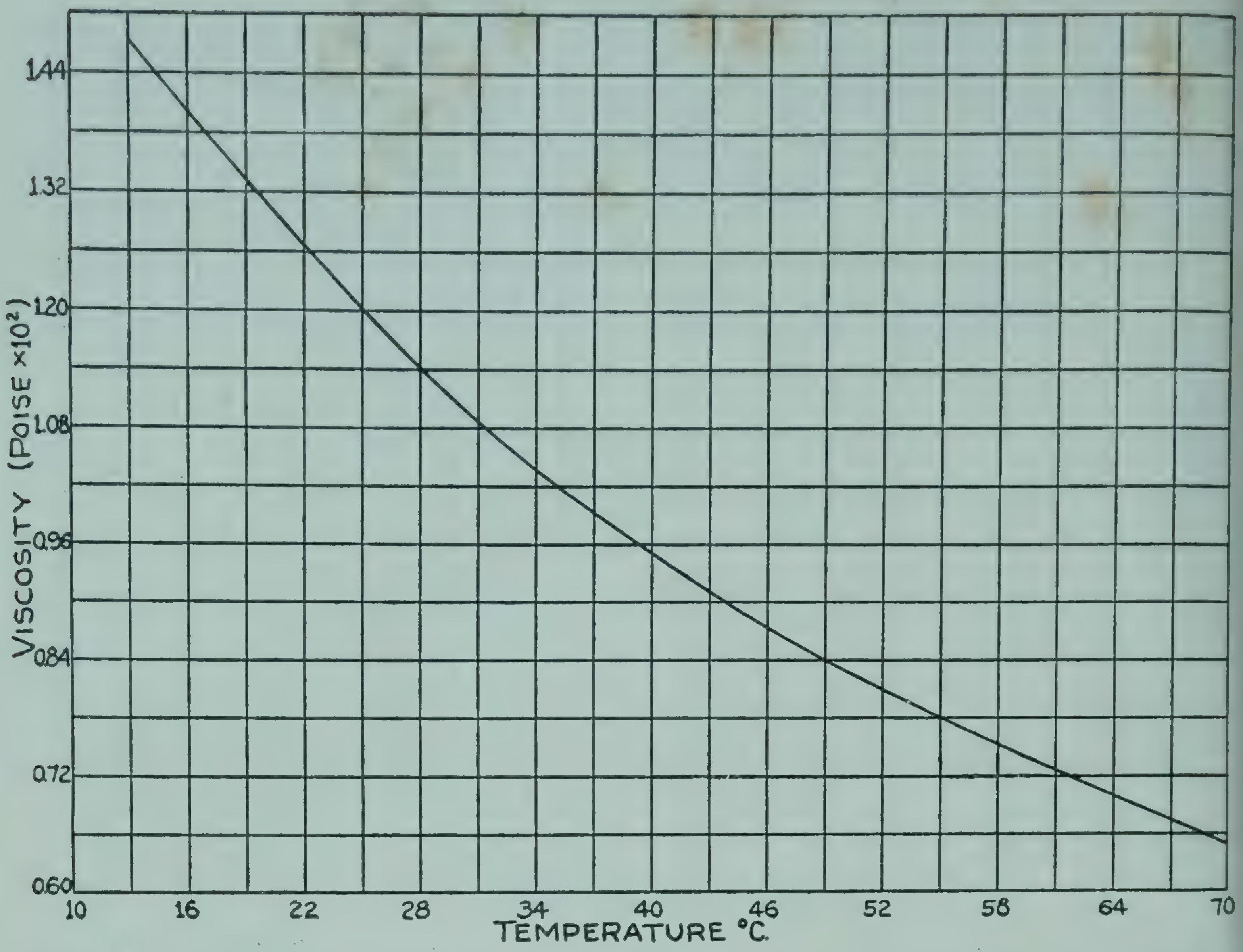


FIGURE 15.64. Viscosity of 1,4-Dioxane at Various Temperatures.[2]

Methylal is available in quantities which justify large scale experimentation and pilot plant development. Celanese' pure methylal holds promise of extensive application in processes that require a low boiling, extremely high power solvent.

As a solvent for plastics and other organic compounds, methylal is superior to ether and acetone in many respects—its relatively high water solubility and ability to be salted out of solution are characteristics of specific value. Its low boiling point (42°C) and stability toward alkalies points to its value as a vaporizing, extraction or reaction solvent.

	Physical Properties	*Tentative Specifications*
Methyl content	100%	95% min.
Color	Water white	Water white
Specific gravity $\frac{20°\ C}{4}$	0.8601	0.8600–0.8630
Flash point, open cup. approx.	0°F	0°F
Boiling point	42.3°C	41.5°–43.5°C
Refractive index, n $\frac{20°\ C}{D}$	1.3534	1.3530–1.3550

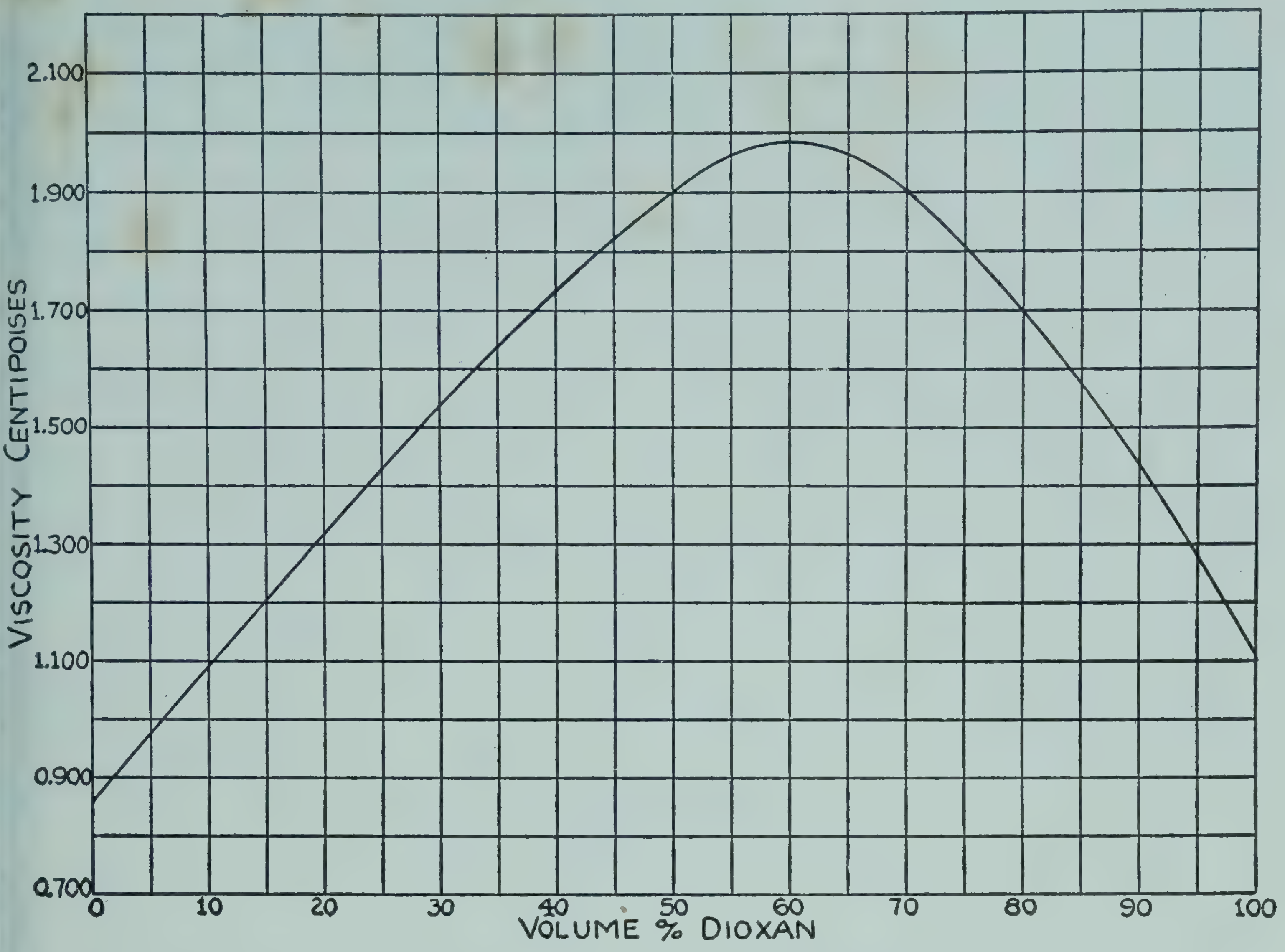
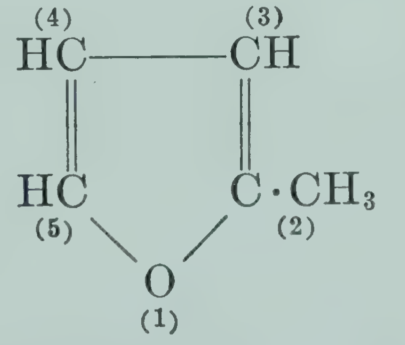


FIGURE 15.65. Viscosity of 1,4-Dioxane-Water Mixtures at 25°C.[2]

2-Methyl Furan:[7] (Sylvan) 2-Methyl furan is a cyclic diene possessing ether-like properties. It is highly reactive with many inorganic and organic compounds yielding a variety of new derivatives which await exploration for the development of commercial applications.



Appearance	Colorless, mobile liquid
Odor	Ether-like
Molecular weight	82.098
Boiling point at 760 mm	62–64°C (144–47°F)
Freezing point	−88°C (−126.4°F)
Specific gravity, 20°C./4°C.	0.915
Index of refraction, N20/D	1.434
Flash point	−30°C (−22°F)
Vapor pressure at 15°C. (59°F)	110.5 mm
20°C. (68°F)	139 mm
25°C. (77°F)	174 mm
30°C. (96°F)	216 mm
Solubility in water at 25°C	Less than 0.3 gm/100 gm.

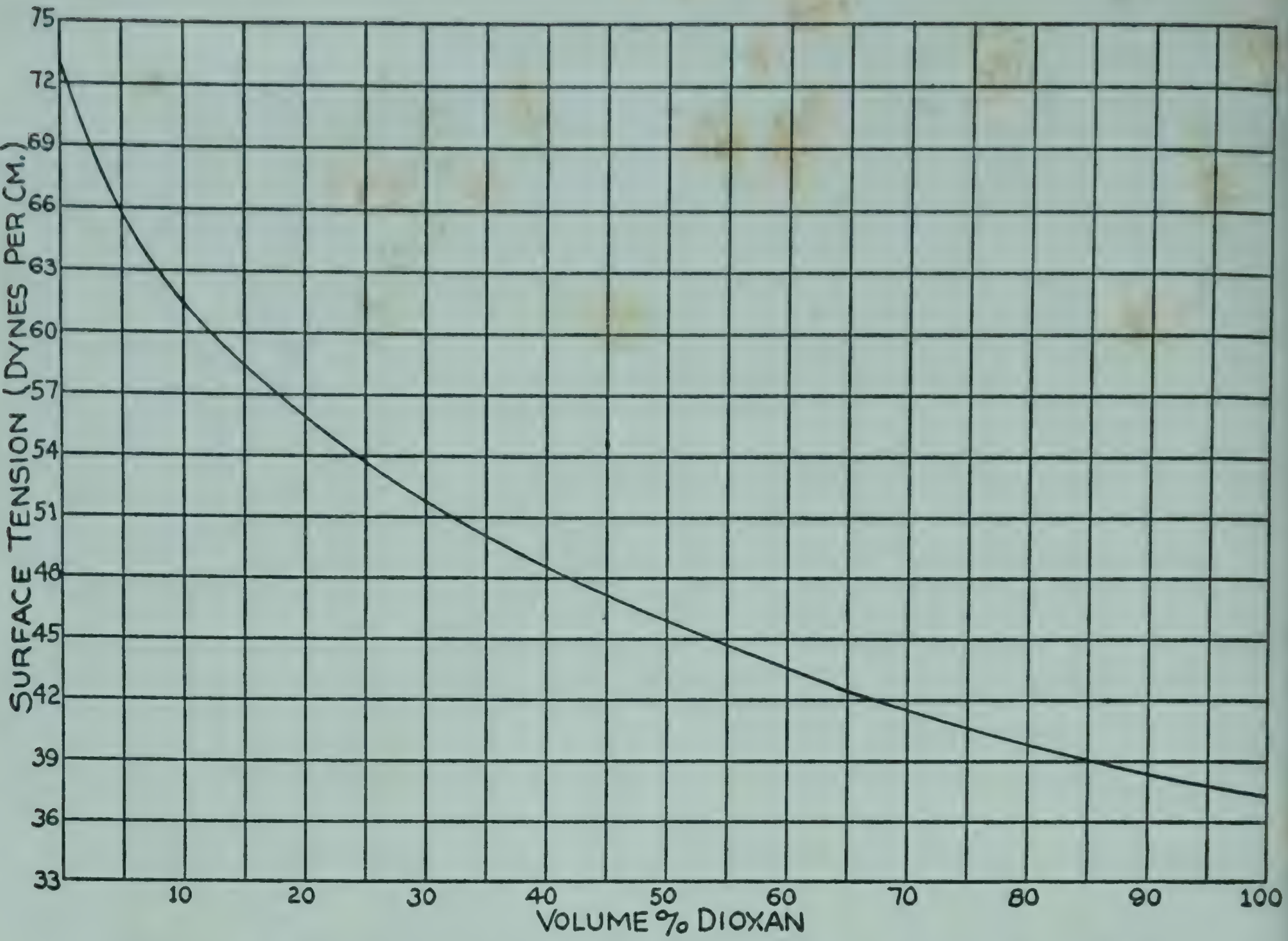


FIGURE 15.66. Freezing Point of 1,4-Dioxane-Water Mixtures at Various Temperatures.[2]

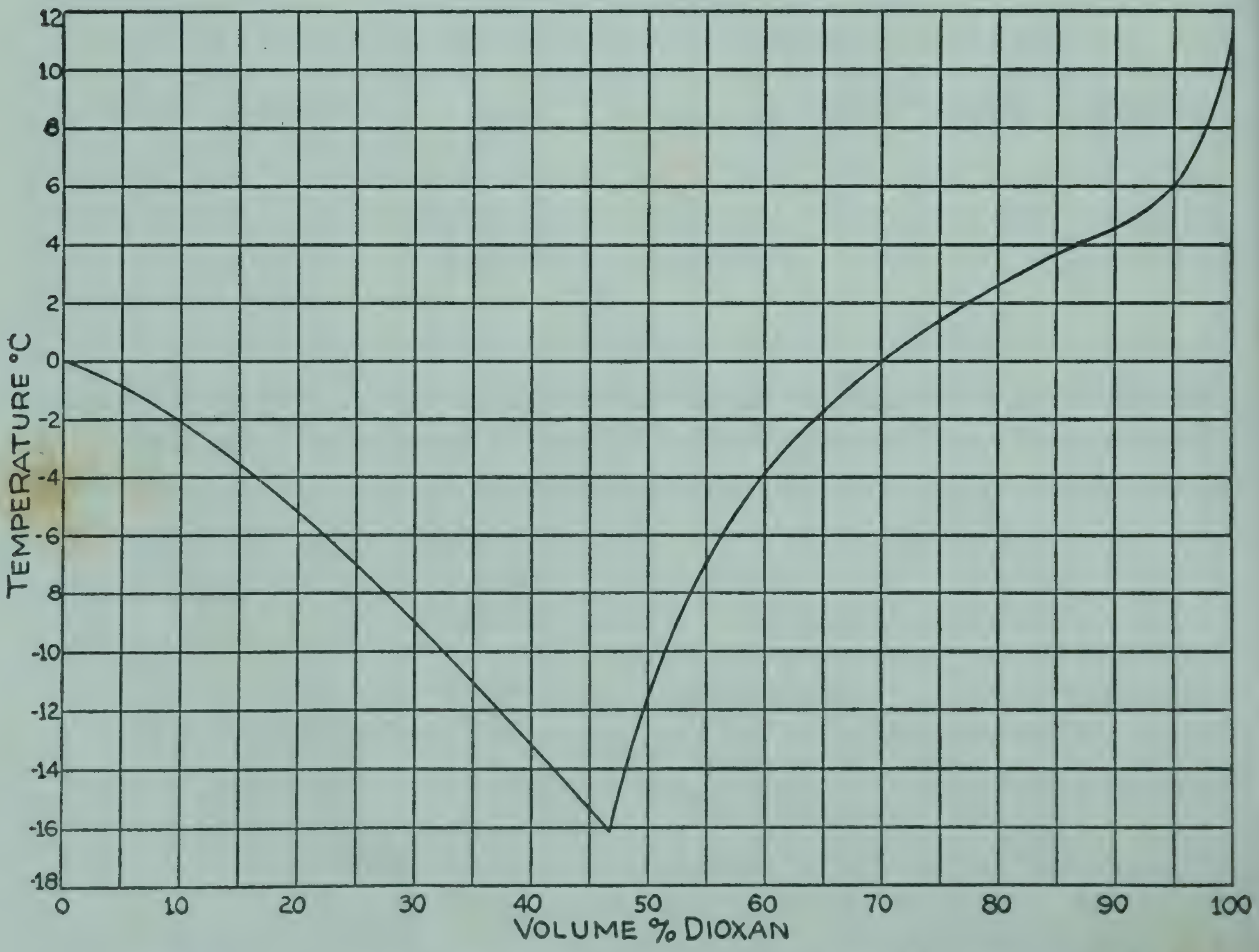
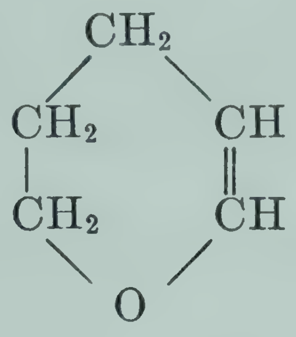


FIGURE 15.67. Surface Tension of 1,4-Dioxane-Water Mixtures at 25°C.[2]

Tetrahydrofurane. Available in pilot plant quantities, this solvent and intermediate is scheduled for quantity production in the near future. Among its many uses, tetrahydrofurane is an exceptional solvent for vinyls and other plastics, and also is an unusual intermediate for the manufacture of adipic and succinic acids and many other compounds.

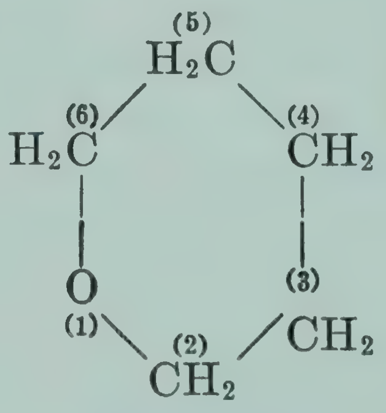
	Physical Properties	*Tentative Specifications*
Color	Water white	Water white
Specific gravity, $\frac{20^\circ C}{4}$	0.8880	0.8840–0.8890
Flash point, open cup,	approx. 70°F	70°F
Boiling point,	66°C	63°–68°C
Refractive index, $n\frac{20^\circ C}{D}$	1.4070	1.4045–1.4075

2:3 Dihydropyran[8]



Physical Properties

	Colorless liquid with characteristic odor
Molecular weight	84.11
Boiling point	85–86°C
Sp., g. $\frac{20^\circ C}{4^\circ C}$	0.923



Pentamethylene Oxide (Tetrahydropyran)[7] Tetrahydropyran reacts with chlorine to form mono-, di-, tri-, and tetrachlorotetrahydropyrans. Reaction with acid chlorides yields omega-haloamyl esters. Conversion to dihalides such as 1,5—dibromopentane and 1,5-dichloropentane can be effected. Ammonia and aliphatic and aromatic amines yield piperidine and substituted piperidines. It is used as a solvent for resins, plastics and rubbers. Lacquers can be made by dissolving certain organic film-forming substances in tetrahydropyran. Solutions of high solids content at a working viscosity can be obtained. A solution of nitrocellulose in tetrahydropyran gives clear, non-blushing films.

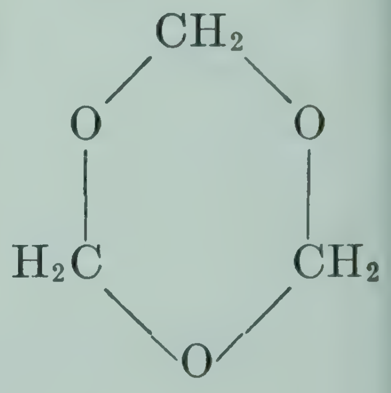
Tetrahydropyran is miscible with water, drying oils and most common organic solvents. The ether-like structure and ability of tetrahydropyran to dissolve a wide range of non-resinous materials suggest its use as a reaction medium for chemical processes such as Grignard reactions.

Physical Properties

Appearance	Colorless, mobile, liquid
Odor	Ether-like
Molecular weight	86.13
Boiling point	88°C at 760 mm
Specific gravity, 20°C/4°C	0.8814
Index of refraction, N20/D	1.420
Flash point	−4°F

Solubility—Miscible with water; less soluble in hot than cold water. Miscible with alcohol, ether, and most common organic solvents.

Trioxane[7] (Cyclic trimeric polymer of formaldehyde)



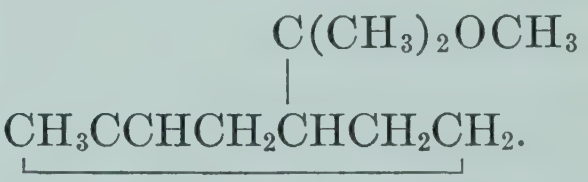
Trioxane is a most unusual chemical. It is an excellent solvent for many classes of materials. Concentrated aqueous solutions of Trioxane have solvent properties which are not possessed by Trioxane itself. Molten Trioxane dissolves numerous organic compounds, such as naphthalene, urea, camphor, dichlorobenzene, etc. It is stable in alkaline or neutral solutions, yet it is depolymerized to formaldehyde by small amounts of strong acid or acid-forming materials. And the rate of depolymerization can be readily controlled.

Trioxane can be used as a source of anhydrous monomeric formaldehyde for reaction with various compounds, such as phenols, amides, amines, proteins, hydrocarbons, and in general, with compounds with which formaldehyde will react in acidic media. It provides means for better control of reaction, better yields and quality of product, shorter reaction time, smoother reaction than is possible with aqueous formaldehyde or other formaldehyde polymers.

Properties

Colorless, crystalline compound	
Molecular weight	90.05
Odor	Mild, Pleasant
Melting point	61°C
Boiling point	115°C
Vapor pressure	
25°C	13 mm
86°C	283 mm
114.5°C	759 mm
129°C	1212 mm
Flash point	45°C
Density (molten) @ 65°C	1.170
Solubility	
Water	Readily Soluble
Alcohols	Readily Soluble
Ketones	Readily Soluble
Ethers	Readily Soluble
Esters	Readily Soluble
Chlorinated Hydrocarbons	Readily Soluble
Aromatic Hydrocarbons	Readily Soluble
Vegetable oils	Readily soluble
Naphthalene	Readily Soluble
Phenol	Readily Soluble
Petroleum ether	Slightly Soluble

Terpinyl Methyl Ether (Terposol No. 3)

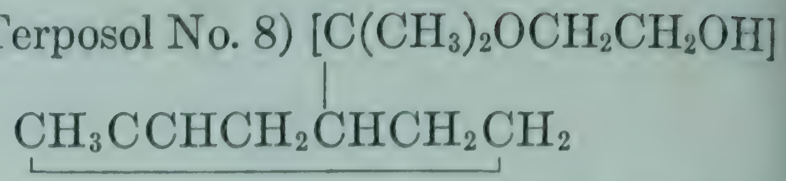


$$\underline{CH_3CCHCH_2\overset{\overset{C(CH_3)_2OCH_3}{|}}{C}HCH_2CH_2}.$$

This terpine ether known as terpinyl methyl ether is a light, colored liquid with a pleasant odor, which contains some impurities. It is a strong solvent for resins and is used in alkyd enamels to the extent of 2 per cent to which it imparts flow.

Aniline point	Below −20°C
Color (Lovibond 500 Amber Series Glasses)	1.0
Distillation range (ASTM)	
5%	215.0°C
50%	216.5°C
90%	217.5°C
95%	218.°C
Flash point (Cleveland open cup)	178°F
Freezing point	Below −10°C
Kauri-Butanol solvency value	Approx. 500
Moisture	0.10%
Refractive index at 20°C	1.4712
Specific gravity at 15.5/15.5°C	0.9192
Viscosity at 25°C (Ubbelohde)	31.8 cp

Terpinyl Ethylene Glycol Ether (Terposol No. 8)



$$\begin{array}{r} [C(CH_3)_2OCH_2CH_2OH] \\ | \quad\quad\quad\quad\quad\quad\quad\quad\quad\quad \\ \underline{CH_3CCHCH_2CHCH_2CH_2} \end{array}$$

Terposol No. 8 is a terpine ether mainly composed of terpinyl ethylene glycol ether. It is a light-colored liquid used in enamels, inks, paints, and varnish.

Aniline point	Below −20°C
Color (Lovibond 500 Amber Series Glasses)	3.0
Distillation range (ASTM) 5%	248.0°C
10%	252.0°C
30%	295.0°C
50%	263.5°C
70%	268.0°C
90%	278.0°C
95%	284.0°C
Flash point (Cleveland open cup)	284°F
Freezing point	Below —10°C
Kauri butane solvency value	Infinite
Moisture	0.05%
Refractive index at 20°C	1.4786
Specific gravity at 15.5/15.5°C	0.9813
Viscosity at 25°C (Ubbelohde)	44.6 cp

Dichlorethyl Ether (2,2′-Dichlorethyl ether, β,β'-dichlorodiethyl ether, chlorex) $[(ClCH_2CH_2)_2O]$. This solvent was first produced commercially on a large scale in 1924. It is a colorless, oily, non-corrosive, stable liquid with a chloroform-like odor. It is miscible with most organic solvents but not with the paraffin hydrocarbons. It is an active solvent for oils, fats, waxes, greases, gums, tars, pectins, natural and synthetic resins, insoluble soaps, and ethyl cellulose. By mixing it with from 10 to 30% ethyl alcohol it will dissolve many types of cellulose esters and ethers. Dichlorethyl ether owes its active solvent power to the combined action of the ethyl ether and ethylene dichloride groups in the molecule. It is used as a spotting agent, a constituent in scouring, boiling-out, mercerizing and kier-boiling baths where it exhibits detergent action, and as a solvent in the refining of lubricating oils. It has other uses in the textile industry as in kier boiling, in peroxide bleaching, in desizing, and as an aid in mercerizing.

Acidity (as hydrochloric)	0.005% by wt, max
Apparent ignition temperature in air	396°C
Boiling point at 760 mm	178.5°C
Boiling range at 760 mm	170–180°C
Coefficient of expansion at 20°C	0.00097 (per °C)
at 55°C	0.00100 (per °C)
Constant boiling mixture (% by wt)	
Dichlorethyl ether	34.4

Water	65.6
b.p. at 760 mm	97.7°C
Flash Point (ASTM, open cup)	79°C
closed cup	55°C
Heat of vaporization at 178°C	64.1 cal/g
Refractive index at 20°C	1.457
Specific gravity at 20/20°C	1.2220
Specific heat (at 20–30°C)	0.369 cal
Surface tension at 25°C	41.8 dynes/sq cm
Solubility in water at 20°C	1.1% by wt
Solubility of water in dichlorethyl ether at 20°C	0.28% by wt
Viscosity at 25°C	2.0653 centipoises
Vapor pressure at 20°C	0.7 mm Hg
Water content	0.10% by wt, max
Weight per gal at 20°C	10.17 lbs

Triglycol Dichloride 2-(2-Chlorethoxy-ethyl 2'-chlorethyl ether) ($ClCH_2CH_2OC_2H \cdot CH_2OCH_2CH_2Cl$). Triglycol dichloride is a water-white liquid which is a solvent for oils, hydrocarbons, rosin, rosin ester, Vinylite resin, and many other substances. It will dissolve nitrocellulose when mixed with alcohol. It finds use as an extractant and because of its low volatility, it is used as a plasticizer.

Acidity (as hydrochloric)	0.010% by wt, max
Boiling point at 760 mm	241.3°C
Boiling range at 760 mm	230–245°C
Color	Water-white
Flash point	250°F
Specific gravity at 20/20°C	1.1974
Solubility in water at 20°C	1.9% by wt
Solubility of water in ether at 20°C	0.83% by wt
Vapor pressure at 20°C	0.06 mm Hg
Water content at 20°C	Miscible without turbidity with 19 vol 60° Be gasoline
Weight per gal at 20°C	9.97 lbs

Glycerine Ethers

Glycerine ethers range widely from low boiling liquids to high-boiling solids. The solubility varies equally from complete water-miscibility to complete water insolubility. The following lists these glyceryl ethers with their density and boiling points. At the present time, these ethers have limited commercial application.

Glyceryl-Ether	*d*	*b.p. (or m.p.) °C*
α-Isoamyl	0.987^{25}_{25}	137-9$_{27}$ 251-2$_{758}$
α, γ—di-Isoamyl	0.903^{25}_{25}	147-53$_{10}$ 269
α-Benzyl	1.196^{15}_{15}	124-6$_{2}$
α-n—Butyl	0.945^{25}_{25}	133-7$_{18}$
Cresyl		
α-Ethyl	1.063	231-2$_{762}$
α, γ-di-Ethyl	0.920_{21}	190
tri-Ethyl	0.886^{25}_{4}	103-5$_{60}$ 181$_{760}$
Epiethylin	0.94_{12}	128-9
Glycidol	1.1143_{25}	41$_{1}$
α-Methyl	1.1147^{25}_{25}	110$_{13}$ 221$_{754}$
β-Methyl		
α, γ-di-Methyl	1.003^{25}_{25}	69.5-70.5$_{15}$ 164-70$_{736}$
tri-Methyl	0.937^{25}_{4}	148$_{765}$
Epimethylin	1.002_{6}	113-4$_{770}$
mono-α-Naphthyl		m.p. 91-2
mono-β-Naphthyl		m.p. 109-10
α-Phenyl		185-7$_{15}$ 150–5$_{4}$ m.p. 53-4
α, γ-di-Phenyl		287-8 m.p. 80-1
α-o-Cl-Phenyl		m.p. 56
α-p-Cl-Phenyl		m.p. 76
mono-2, 4-di-Nitrophenyl		m.p. 83
Epiphenylin	1.08^{25}_{4}	115-6$_{3\text{-}4}$
α-Propyl	1.074^{18}_{4}	118-22$_{15}$
α, γ-di-Isopropyl	0.915_{15}	112-3
α, γ-di-n-Propyl		215–7
mono-p-Tolyl		m.p. 73-4

Glyceryl α-monomethyl Ether (α-Monomethyl ether of glycerine) ($CH_3OCH_2CHOHCH_2OH$). Glyceryl α-monomethyl ether is a colorless liquid, soluble in benzene, ethyl alcohol, glycerol and water but insoluble in gasoline and carbon tetrachloride. It is a solvent for rosin, and when mixed with butyl acetate is compatible with nitrocellulose. It may be used as a selective solvent and in the manufacture of alkyd resins.

Boiling range at 745 mm	90% between 215–220°C
Refractive index, $n \frac{25°}{D}$	1.442
Specific gravity at 25/25°C	1.1147
Weight per gal	9.29 lbs

Glyceryl α,γ-Dimethyl Ether (α,γ-Dimethyl ether of glycerine) (H_3C-$OCH_2CHOHCH_2OCH_3$). Glycerine α,γ-dimethyl ether is a water-white liquid soluble in benzene, gasoline, carbon tetrachloride, ethyl alcohol, water, and glycerine, but insoluble in linseed oil and other fixed oils. It is a solvent for rosin, cellulose acetate and when mixed with butyl acetate, is compatible with nitrocellulose. It has use as a solvent and plasticizer.

Boiling range at 736 mm.	90% between 164–170°C
Specific gravity at 25/25°C	1.003
Weight per gal	8.36 lbs

Glyceryl α mono-*n*-Butyl Ether (α-Mono-n-butyl ether of glycerine) ($C_4H_9OCH_2CHOHCH_2OH$). α-Mono-n-butyl ether of glycerine is a colorless liquid, soluble in benzene, gasoline, ethyl alcohol and carbon tetrachloride, but only slightly soluble in water and glycerol. It is a solvent for rosin and ester gum and may be used in the preparation of varnishes made with these substances.

Boiling range at 18 mm.	90% between 133–137°C
Refractive index, $n \frac{25°}{D}$	1.434
Specific gravity at 25/25°C	0.945
Weight per gal	7.87 lbs

Glyceryl α-Monoisoamyl Ether (α-Monoisoamyl ether of glyceryl) ($C_5H_{11}OCH_2CHOHCH_2OH$). α-Monoisoamyl ether of glyceryl is a colorless liquid which generally contains small amounts of other amyl isomers. It is soluble in benzene, ethyl alcohol, halogenated hydrocarbons, carbon tetrachloride, gasoline, linseed oil, and other fixed oils and, in certain amounts, soluble in glycerol and water. It is a solvent for rosin and, when mixed with butyl acetate, is compatible with nitrocellulose. It may be used as a solvent, in the preparation of alkyd resins and in the synthesis of ester derivatives.

Boiling range at 745 mm	90% between 252–260°C
Refractive index, $N \frac{25°}{D}$	1.442
Specific gravity at 25/25°C	0.987
Weight per gal	8.22 lbs

Glyceryl α,γ Diisoamyl Ether (α,γ-Diisoamyl ether of glycerine) ($C:H_{11}OCH_2CHOHCH_2OC:H_{11}$). Glyceryl α,γ diisoamyl ether is a water-white liquid which may contain small quantities of other amyl isomers. It is soluble in ethyl alcohol, benzene, gasoline, carbon tetrachloride, and linseed oil, but insoluble in water and glycerol. It is a solvent for ester gum and rosin and has use as a solvent and plasticizer.

Boiling range at 10 mm	90% between 147–153°C
Refractive index, $n \frac{25^\circ}{D}$	1.432
Specific gravity at 25/25°C	0.903
Weight per gal	7.52 lbs

Miscellaneous Alkyl Aryl Ethers

These ethers are generally high boiling, water insoluble liquids of pleasant odor, miscible with a variety of organic solvents and commercial oils, fats, waxes, and resins.

Physical Properties

	Formula	Boiling Range °C	Flash Point °F	Sp. Gravity 20/20	Molecular Wt.
Methyl Phenyl Ether (Anisole)	$CH_3OC_6H_5$	150–160	120	0.993	
n-Butyl Phenyl Ether	$C_4H_9OC_6H_5$	202–212	180	0.929	
Amyl Phenyl Ether	$C_5H_{11}OC_6H_5$	214–229	185	0.924	164.1
p-tert-Amylphenyl Methyl Ether	$C_5H_{11}C_6H_4OCH_3$	239–243	210	0.942	
p-tert-Amylphenyl-*n*-Amyl Ether	$C_5H_{11}C_6H_4OC_5H_{11}$	285–295	260	0.905	234.2
Amyl Benzyl Ether	$C_5H_{11}OCH_2C_6H_5$	224–239	175	0.912	
Amyl Tolyl Ether	$C_5H_{11}OC_6H_4CH_3$	240–264	195	0.916	
Amyl beta Naphthyl Ether	$C_5H_{11}OC_{10}H_7$	320–350	310	1.01	
Amyl Xylyl Ether	$C_5H_{11}OC_6H_3(CH_3)_2$	250–263	205	0.907	

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1. U. S. Industrial Chemicals, Inc., New York, N. Y.
2. Carbide & Carbon Chemical Corporation, New York, N. Y.
3. Watson, P. D., *Ind. Eng. Chem.*, **32:** 399 (1940).
4. *Ind. Eng. Chem.*, News Ed., **14:** 305 (1936).
5. Dow Chemical Co., Midland, Mich.
6. Cellanese Corp. of America, New York, N. Y.
7. E. I. du Pont de Nemours & Co., Inc., Wilmington, Del.
8. Imperial Chemical Industries, Ltd., London, England.

Chapter 16

Esters

Methyl Acetate (Ch_3COOCH_3). Methyl acetate is a water-white flammable, readily hydrolysable liquid, with a fragrant odor. This low-boiling solvent was first prepared in 1835 by reacting acetic acid and methanol. It is miscible with most organic solvents and will completely dissolve cellulose nitrate and acetate, ethyl cellulose, resins such as ester gum, rosin, cumar, elemi, phenolics, and oils such as corn, linseed, castor, neatsfoot, chinawood and cottonseed. It will only partially dissolve shellac, manila, dammar, pontianac, Beckacites, and alkyds. In many respects, methyl acetate resembles acetone as a solvent particularly as to its boiling point, solvent power and miscibility, but its tendency to hydrolyze to methanol and acetic acid, in the presence of water limits its wider use in the industries. Methyl acetate is usually admixed with higher boiling solvents. It is used in lacquers, paints, varnishes, enamels, perfumes, dyes, dopes, plastics, and synthetic finishes as well as a substitute for acetone.

Acidity (as acetic)	0.005%, max
Boiling point	56.9°C
Distillation range	55–58°C
Coefficient of expansion (per °C) at 20°C	0.001390
Color	Water-white
Critical temperature	233.7°C
Critical pressure	46–3 atm
Dielectric constant at 20°C	7.3 ± 0.2
Dilution ratios	
Toluene	2.9
Petroleum naphtha	0.9
Electrical conductivity at 25°C	3.4×10^{-6} mho
Flash point (A.S.T.M. Open Cup)	−15°C
Freezing point	−98.1°C
Heat of combustion	5371 cal/g
Heat of vaporization	104.4 cal/g
Non-volatile matter	0.005 gram per 100 cc, max
Refractive index at 20°C	1.3593
Solubility in water at 20°C	24% by wt
Solubility of water in solvent at 20°C	8% by wt
Specific gravity at 20/20°C	0.9353
Surface tension at 20°C	24.6 dynes/cm
Vapor pressure at 20°C	173 mm Hg
Viscosity at 20°C	0.00381 poises
Weight per gal at 20°C	7.783 lbs

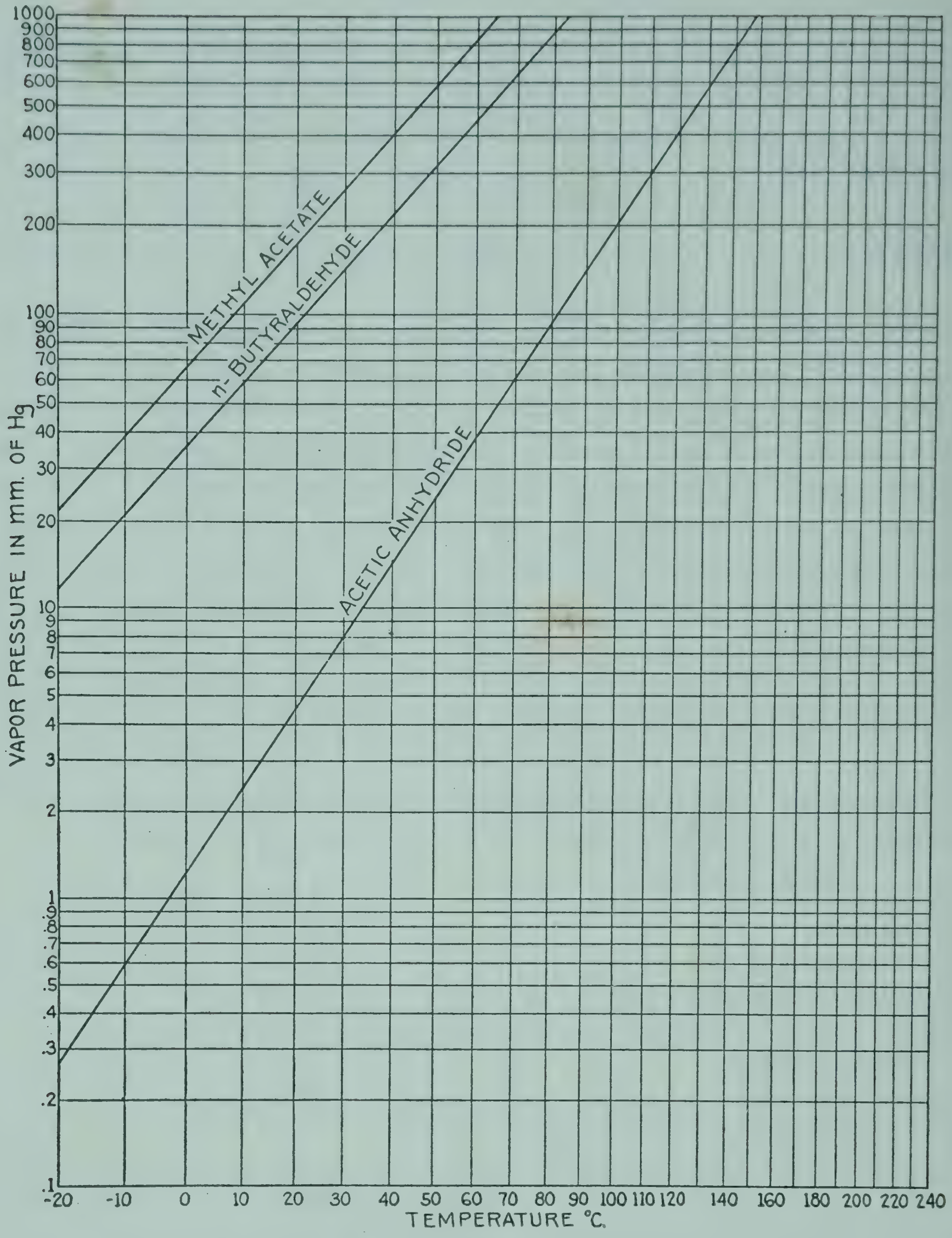


FIGURE 16.1. Vapor Pressures.

Azeotropic Mixtures

	% by Wt		% by Wt	B.P. °C
Methyl Acetate	44.9	Acetone	55.1	56.1
Methyl Acetate	29.9	Carbon Disulfide	70.1	40.1
Methyl Acetate	81.1	Methanol	18.9	54.0

Ethyl Acetate (Acetic Ether) ($CH_3COOC_2H_5$). Ethyl acetate is a water-white, flammable liquid with a pleasant, fruity odor. The 85 to 88 per cent grade of ethyl acetate suitably denaturated is generally used for com-

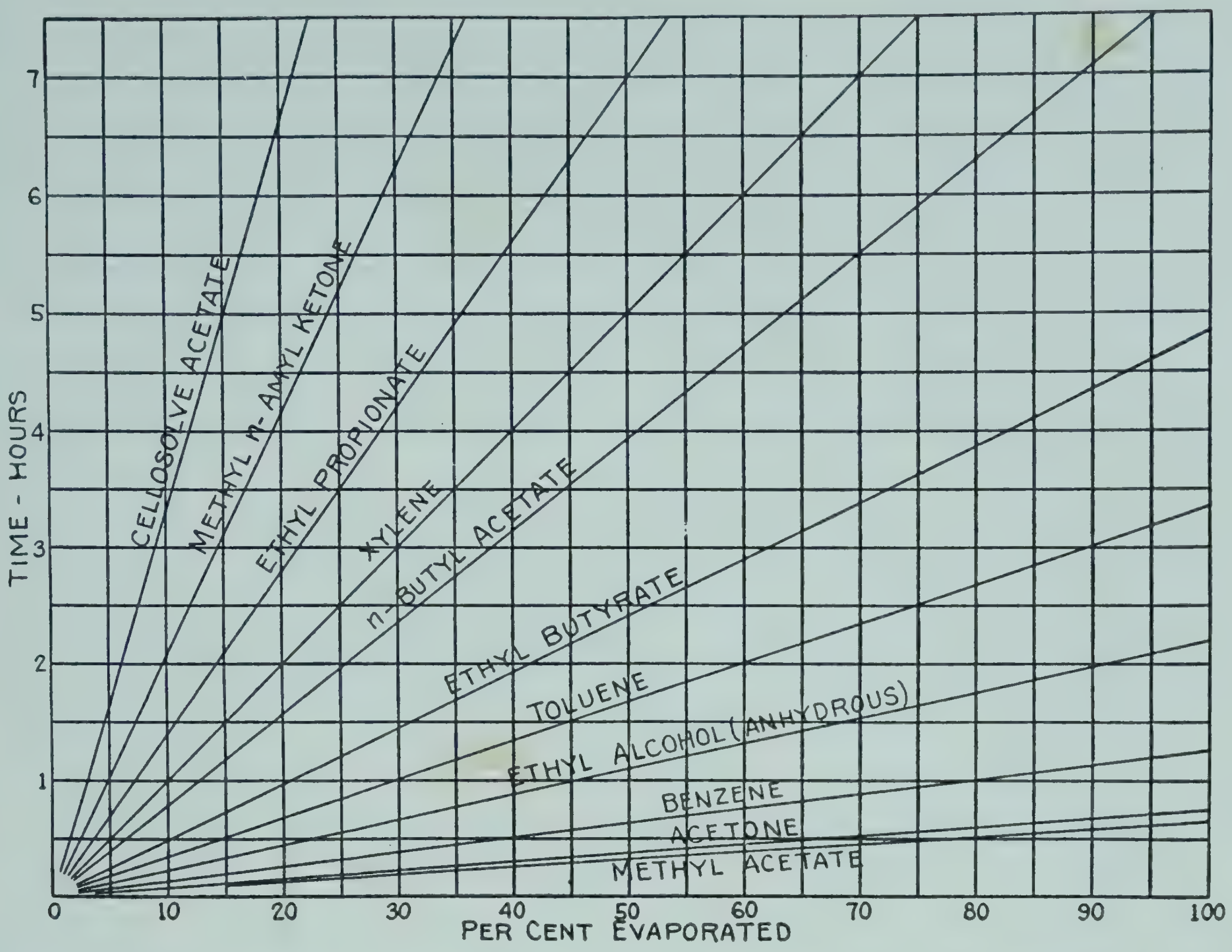


FIGURE 16.2. Comparative Rates of Evaporation (Atmospheric Conditions).

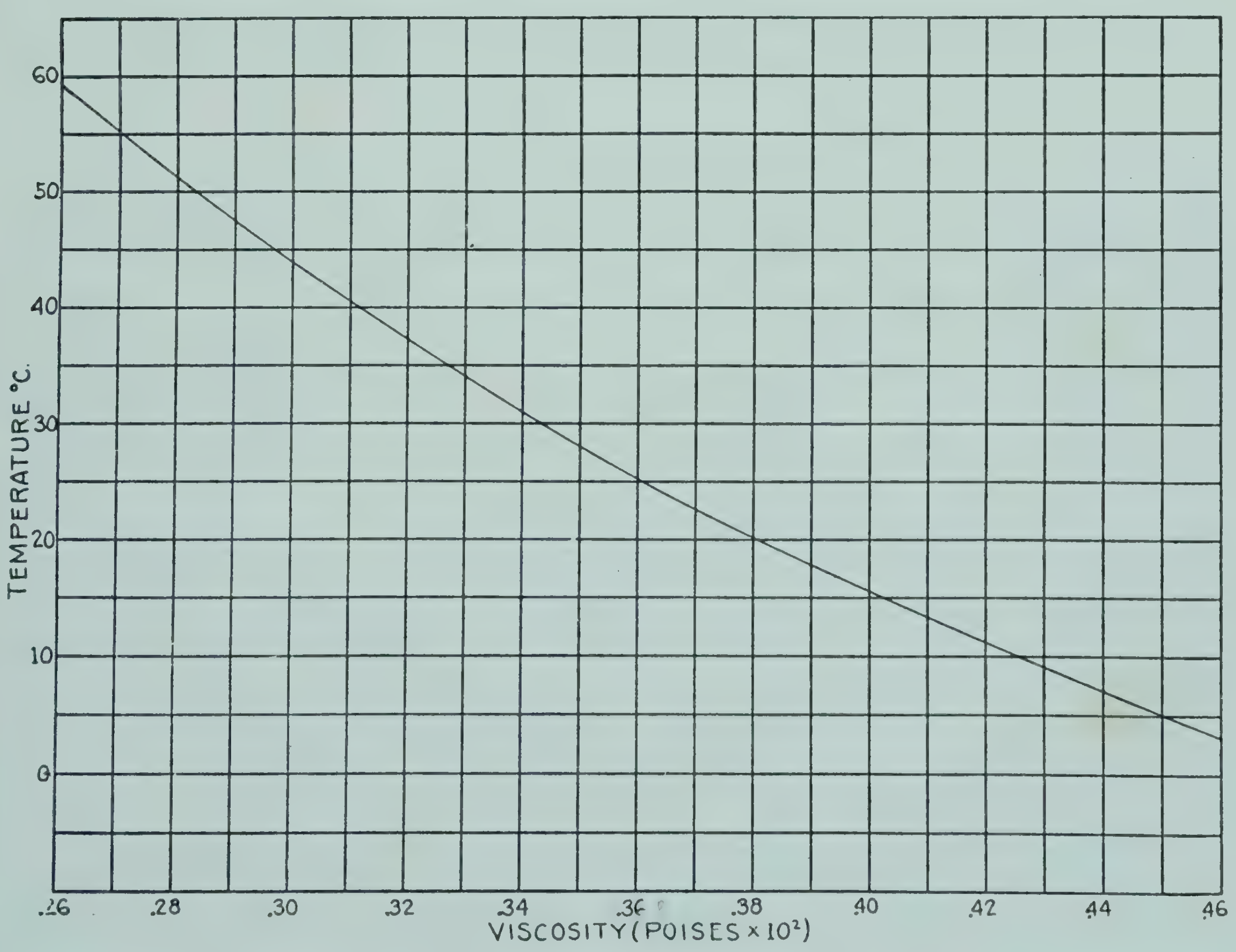


FIGURE 16.3. Viscosity of Methyl Acetate at Various Temperatures.

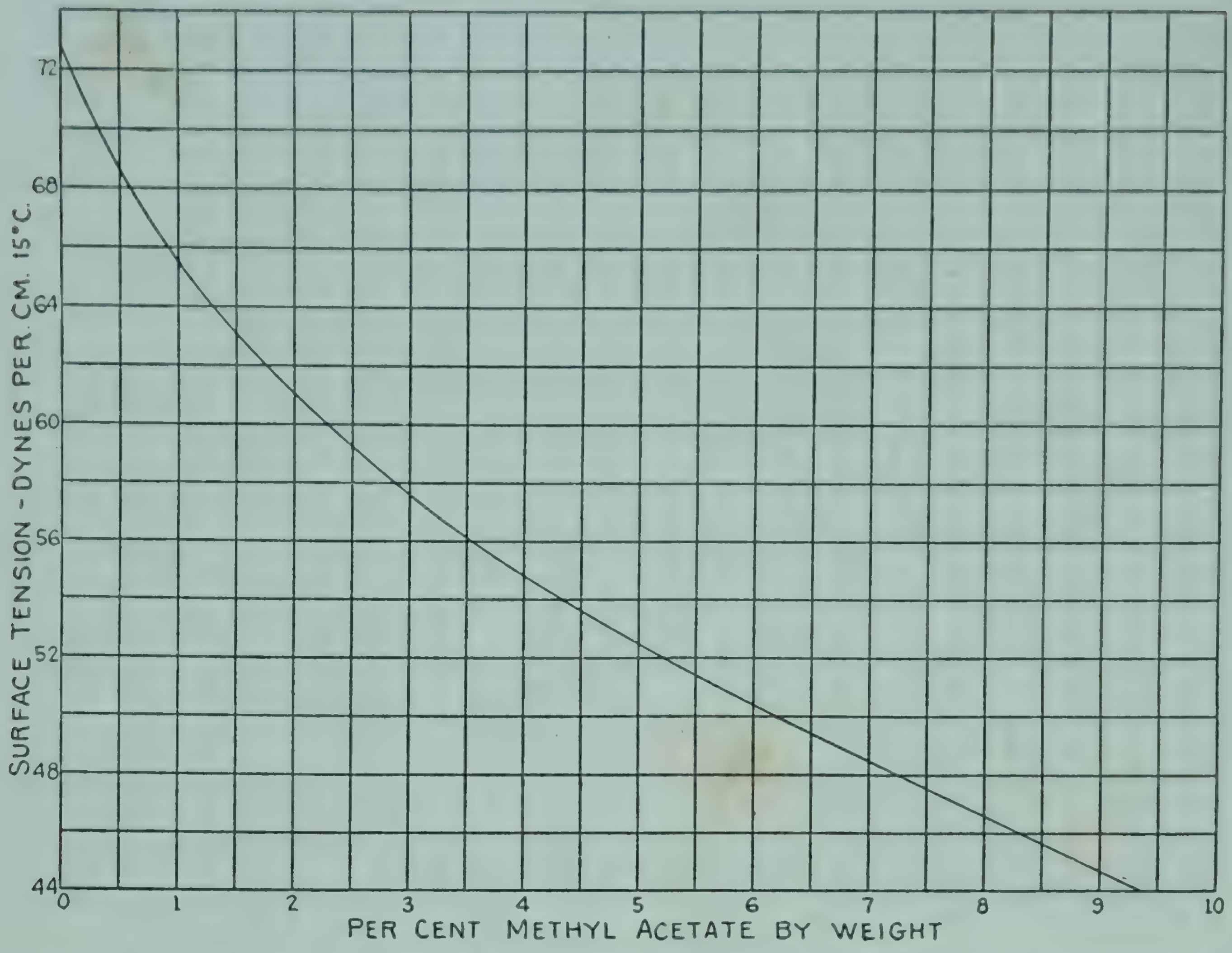


FIGURE 16.4. Surface Tension of Aqueous Solutions of Methyl Acetate at 15°C.

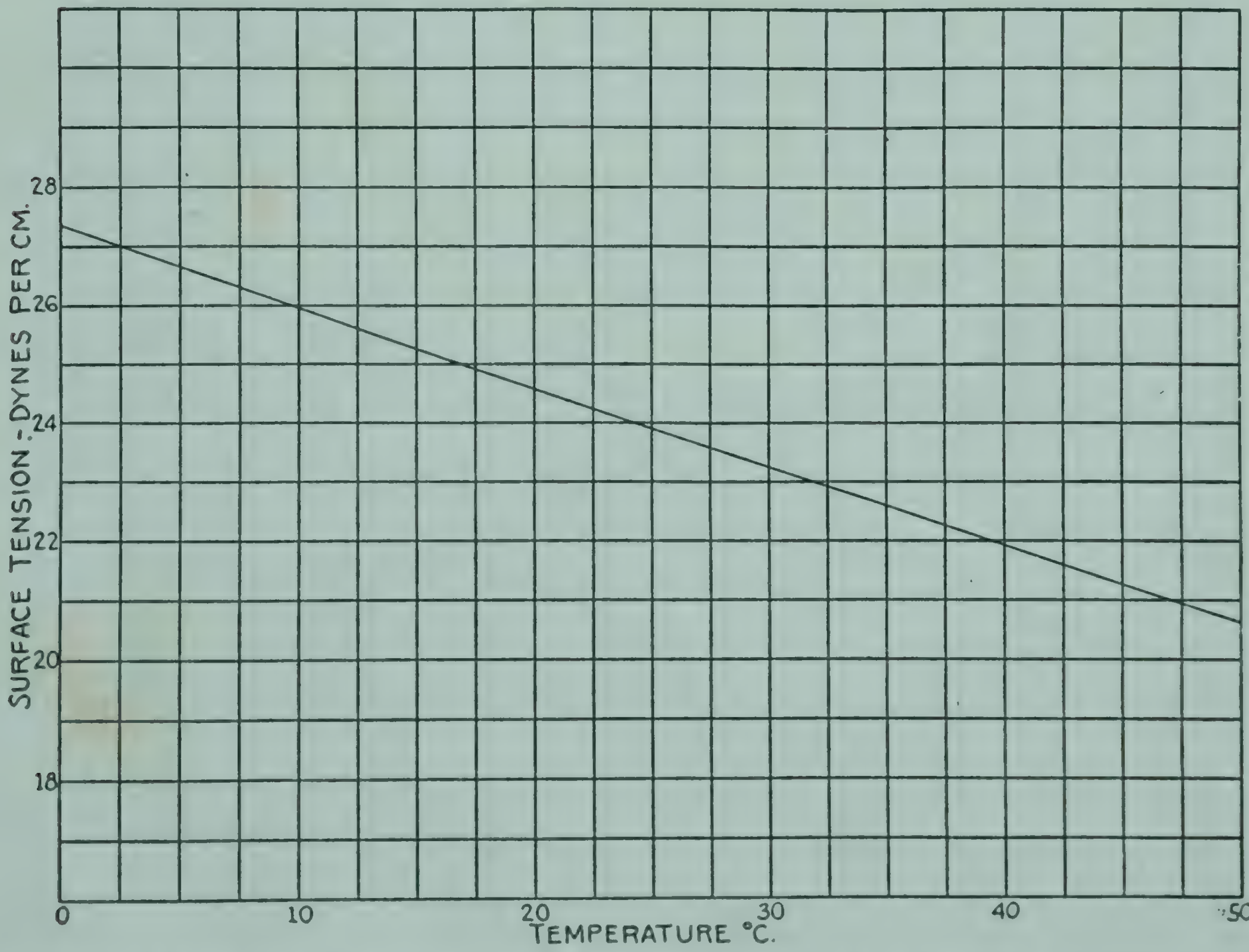


FIGURE 16.5. Surface Tension of Methyl Acetate at Various Temperatures.

mercial purposes but 95 and 99% grades are also available. It is miscible with most organic solvents such as alcohols, ketones, esters, aromatic, aliphatic, and halogenated hydrocarbons. It dissolves such materials as nitrocellulose, camphor, oils, fats, waxes, gums, and natural and synthetic resins. It will tolerate fairly large amounts of lacquer diluents and like methyl acetate it not only has a wide range of solubilities but it possesses the unique property of dissolving nitro cellulose cellulose acetate and cellulose ethers yielding solutions of low viscosity. Its solvent power for cellulose derivatives is much improved however by adding a small quantity of alcohol.

Considered as one of the best low-boiling solvents for nitrocellulose, ethyl acetate is used extensively in the lacquer industry in the manufacture of lacquers, dopes and cements, also in the preparation of varnishes, coated paper, transparent wrapping paper, polishes, plastics and varnish removers. Other uses for ethyl acetate are in organic synthesis, in the manufacture of esters, and pharmaceuticals. As a solvent ethyl acetate finds commercial application in the extraction of acetic acid from dilute aqueous solutions, in flavors, candy glazes, smokeless powder and cleaning preparations. Principal applications are outlined in the wartime end-use pattern below.

ALLOCATIONS OF ETHYL ACETATE: JULY 1, 1944–JUNE 30, 1945
(*Thousands of pounds of 85% pure*)

USE	TOTAL		JAN. 1–JUNE 30, 1945	JULY 1–DEC. 31, 1944
	Amount	Per cent		
Total Allocations	124,172	100.0	64,511	59,661
Export	9,843	8.0	5,100	4,743
Other uses	114,329	92.0	59,411	54,918
Protective coatings[1]	78,502	63.2	39,675	38,827
Chemical manufacture	7,168	5.8	3,478	3,690
Ethyl acetoacetate	5,936	4.8	2,768	3,168
Acetic acid concentrate	1,232	1.0	710	522
Plastics	4,982	4.0	2,465	2,517
Denaturants	4,963	4.0	2,687	2,276
Adhesives and cements	4,825	3.9	3,204	1,621
Drugs and pharmaceuticals	2,783	2.2	1,607	1,176
Smokeless powder	1,028	0.8	728	300
Cleaners and removers	995	0.8	441	554
Impregnated oil seals	755	0.6	517	238
Resins	357	0.3	221	136
Aircraft cleaning	244	0.2	46	198
Food flavors	145	0.1	139	6
Research	89	0.1	55	34
Miscellaneous uses and small orders	7,493	6.0	4,148	3,345

[1] For military and industrial equipment and furniture.

	(85 to 88%)
Acidity (as acetic acid)	0.01% by wt, max
Blush resistance at 90°F (10% $\frac{1}{2}$ sec. R.S. nitrocellulose solution)	Clear 45% Relative humidity Bluish 50%
Coefficient of cubical expansion (ordinary temperatures)	0.00073 per °F 0.00132 per °C
Color	Water-white
Critical temperature	250.1°C
Critical pressure	37.8 atmospheres
Dilution ratio	
Toluol	3.5
Petroleum naphtha	1.1
Distillation range	Below 70°C None Below 72°C Not more than 10% Above 80°C None
Dryness	Miscible without turbidity with 20 volumes 60° Bé gasoline at 20°C
Electrical conductivity at 25°C	Less than 1×10^{-9} reciprocal ohms
Evap. rate at 95°F (in min.)	
5%	$\frac{1}{4}$
25%	$1\frac{1}{2}$
50%	$3\frac{3}{4}$
75%	$6\frac{3}{4}$
90%	$9\frac{1}{2}$
95%	$11\frac{1}{4}$
Flash point	−5°C (23°F)
Freezing point	−82.4°C
Non-volatile matter	0.003 gram per 100 cc, max
Refractive index at 20°C	1.3725
Solubility in water at 25°C	9.7% by vol
Solubility of water in solvent at 25°C	9.8% by vol
Specific gravity at 20/20°C	0.883 to 0.888
Viscosity at 20°C	4.546 millipoises
Weight per gal at 68°F	7.36 lbs

	(95 to 98%)
Acidity (as acetic)	0.01% by wt, max
Blush resistance at 90°F (10% $\frac{1}{2}$ sec. R.S. nitrocellulose solution)	Clear 50% Relative humidity Blush 55%
Coefficient of expansion per 1°F	0.00074
per 1°C	0.00133
Color	Water-white
Dilution ratio	
Toluol	3.2

Petroleum hydrocarbon	1.0
Distillation range	74 to 80°C
Dryness at 20°C	Miscible without turbidity with 20 vol 60° Bé gasoline
Evap. rate at 95°F (in min.	
5%	¼
25%	1½
50%	3½
75%	6
90%	7¾
95%	8½
Flash point	26°F (approximate)
Non-volatile matter	0.003 gm per 100 cc, max
Solubility of water in solvent at 25°C	4% by vol
Specific gravity at 20/20°C	0.895 to 0.900
Viscosity (10% ½ sec. nitrocellulose solution)	33 centipoises
Water	No turbidity when mixed with 19 volumes of 60° Bé gasoline at 20°C
Weight per gal at 20°C	7.47 lbs

(99 to 100%) acetic ether grade

Acidity (as acetic)	0.01% by wt, max
Blush resistance at 90°F (10% ½ sec. R.S. nitrocellulose solution)	Clear 55% Relative humidity Blush 60%
Coefficient of expansion per 1°F	0.00074
per 1°C	0.000133
Color	Water-white
Dilution ratio	
Toluol	3.0
Petroleum naphtha	1.0
Distillation range	75 to 80°C
Electrical conductivity at 25°C	3.2×10^{-7} recip ohms
Evap. rate at 95°F (in min.)	
5%	¼
25%	1½
50%	3¾
75%	6½
90%	9¼
95%	10¼
Explosive limits	2.26–11.4%
Flash point	0.5°C
Freezing point	−82.4°C
Heat of combustion	538 kg. cal/mole
Heat of vaporization at 0°C	102 cal/gm
at 80°C	102.9 cal/gm
Non-volatile matter	0.003 gram when 100 cc, max

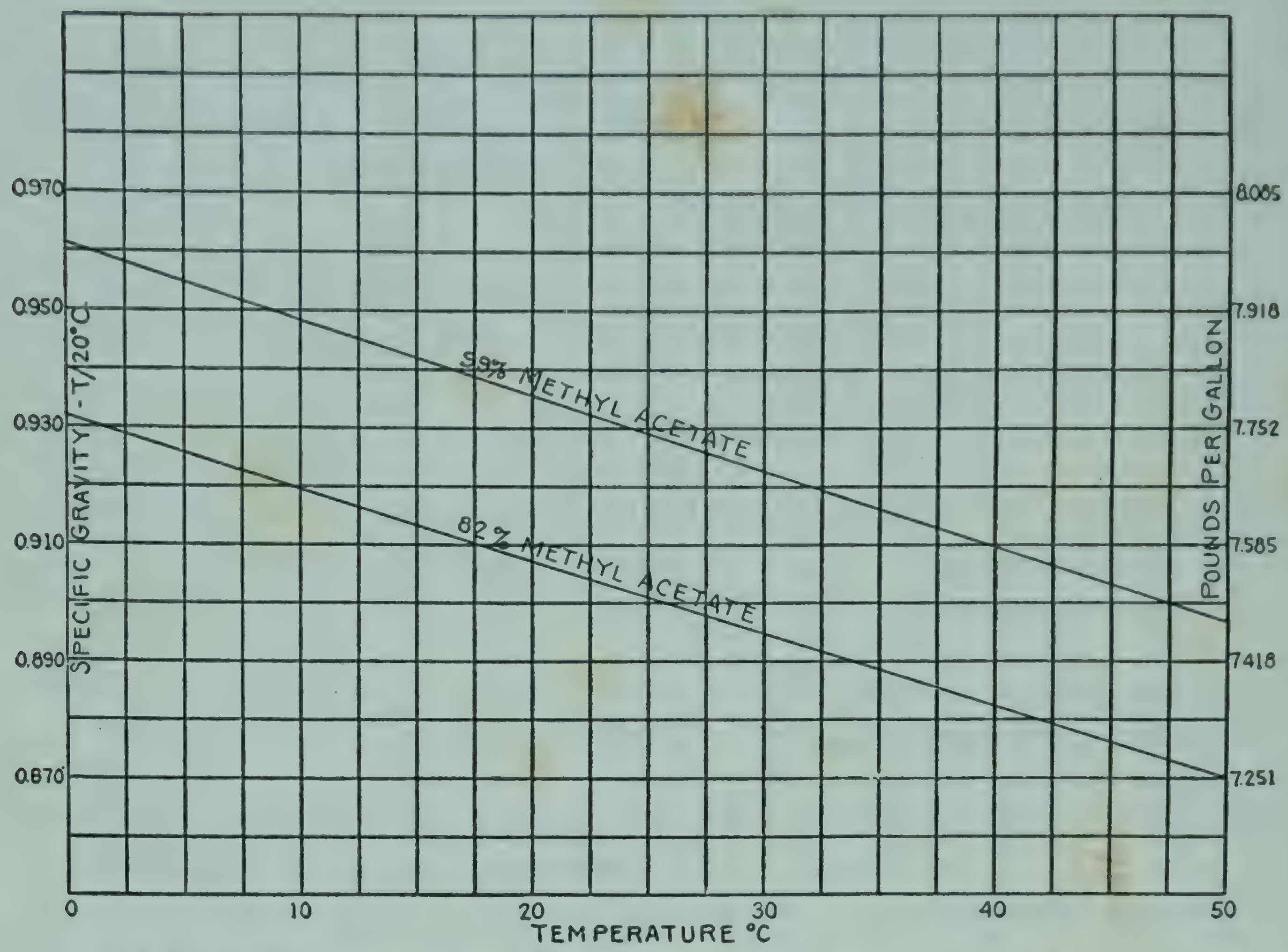


FIGURE 16.6. Specific Gravity and Weight per Gallon of Methyl Acetate at Various Temperatures.

(99 to 100%)

Refractive index at 19°C	1.3722
Solubility in water at 20°C	7.9% by wt
Solubility of water in solvent at 20°C	3.0% by wt
Specific gravity at 20/20°C	0.899 to 0.902
Surface tension at 20°C	24.3 dynes/cm
Viscosity at 21.4°C	0.00442 poises
Vapor pressure at 20/20°C	72.8 mm Hg
Weight per gal at 20°C	7.5 lbs

Azeotropic Mixtures

	% by Wt		% by Wt	B.P. °C
Ethyl Acetate	74.0	Tert.Butanol	26.0	75.2
	43.1	Carbon Tetrachloride	56.9	74.8
	69.2	Ethanol	30.8	71.8
	77.0	Isopropanol	23.0	74.8
	20.0	Methanol	80.0	62.3
	93.9	Water	6.1	70.4

Ternary Mixtures

		B.P.
Ethyl Acetate	80.9%	
Ethanol	8.8%	
Water	10.3%	70.3°C

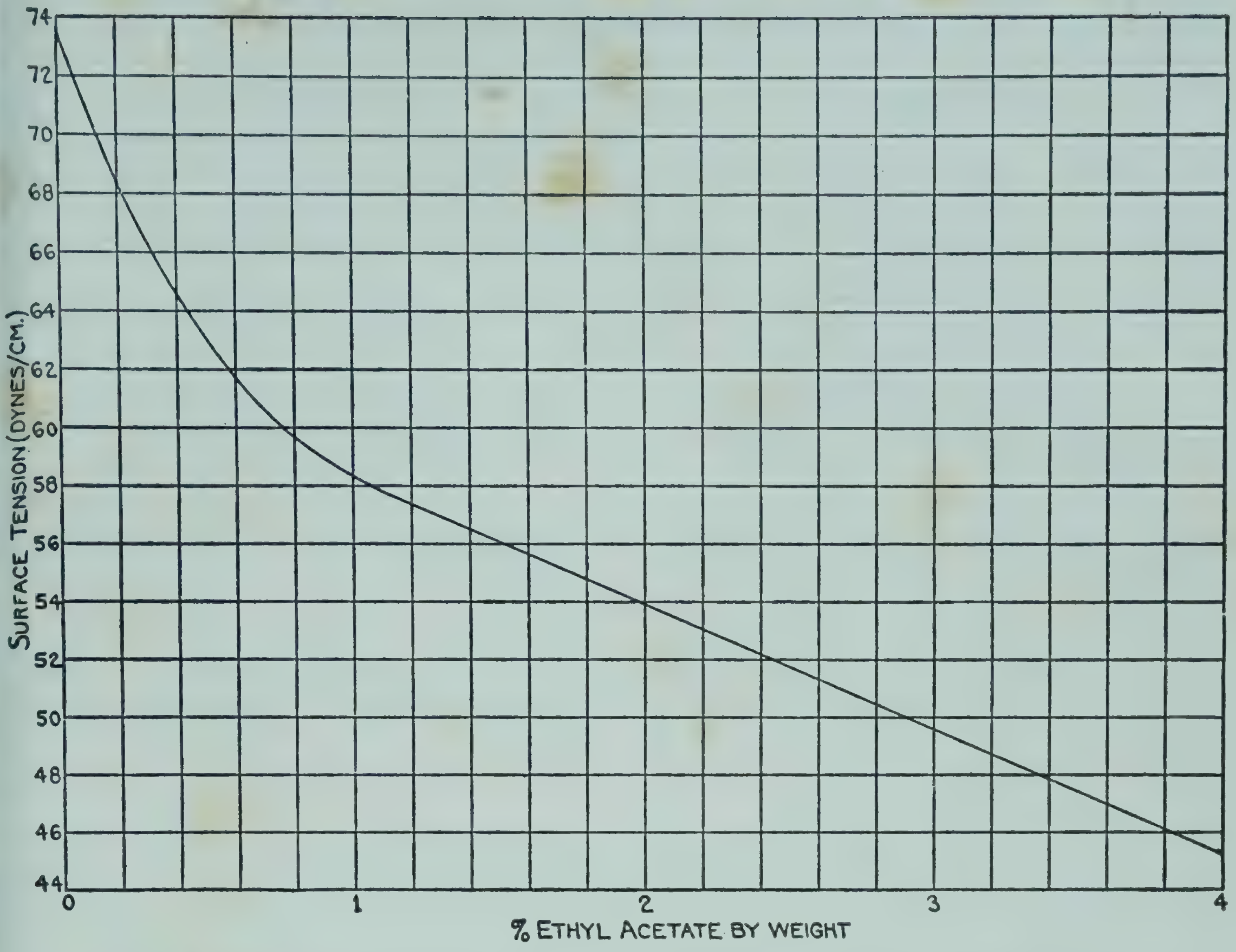


Figure 16.7. Surface Tension of Aqueous Solutions of Ethyl Acetate (20°C).[1]

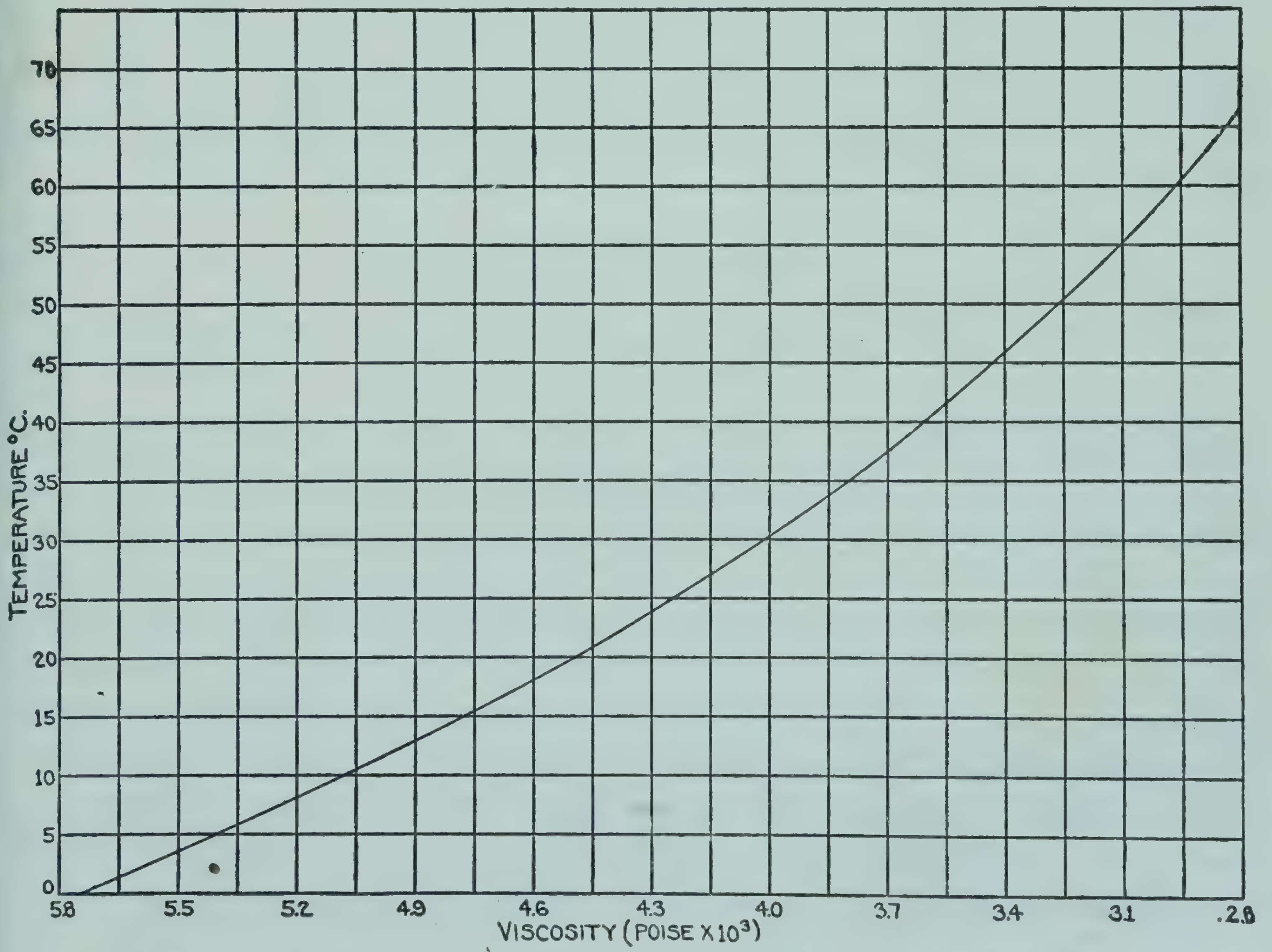


Figure 16.8. Viscosity of Ethyl Acetate at Various Temperatures.

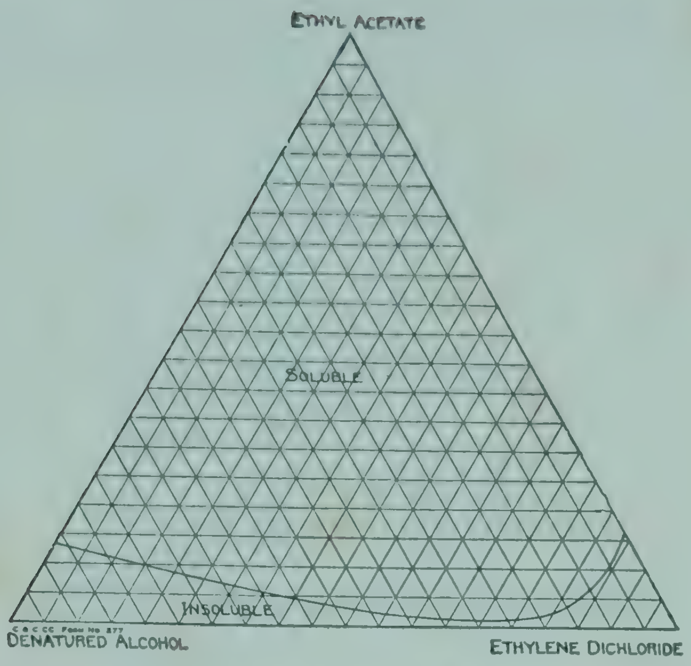


Figure 16.9. Solubility of $\frac{1}{2}$-Second R. S. Nitrocellulose in Mixtures of Ethyl Acetate, Ethylene Dichloride, and Denatured Alcohol.[1]

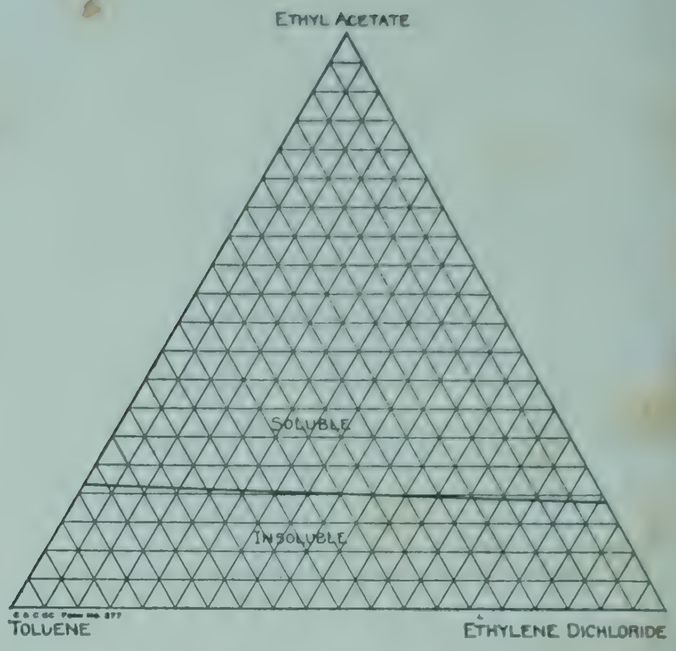


Figure 16.10. Solubility of $\frac{1}{2}$-Second R. S. Nitrocellulose in Mixtures of Ethyl Acetate, Toluene, and Ethylene Dichloride.[1]

***n*-Propyl Acetate** ($CH_3COOC_3H_7$). The properties of *n*-propyl acetate are, approximately, intermediate between those of ethyl and *n*-butyl acetates. It is miscible with alcohols, ketones, esters, oils and hydrocarbons and is a good solvent for nitrocellulose and a wide range of cellulose derivatives, especially when it is admixed with the aromatic hydrocarbons or the lower aliphatic alcohols. It will also dissolve natural and synthetic resins like elemi, cumar resins, ester gum, manila, mastic, rosin and sandarac. It is used principally as a low boiling component in nitrocellulose lacquer formulations.

Boiling point	101.6°C
Flash point	12°C
Specific gravity	0.897

Isopropyl Acetate ($CH_3COOCH(CH_3)_2$). Isopropyl acetate is a water-white pleasant odored liquid with properties intermediate between ethyl and butyl acetates. It is miscible with most of the common organic solvents, such as alcohols, ketones, esters, oils, hydrocarbons, etc., and it is a solvent for nitrocellulose, cellulose acetate (of low viscosity) and a wide range of oils, fats, waxes, gums, and natural and synthetic resins. Like *n*-propyl acetate, its solvent-power for cellulose esters is increased when lower aliphatic alcohols are added. It is largely used in the lacquer industry where its slow evaporation rate and blush resistance are of importance. It is also used in the manufacture of plastics, artificial leather, dopes, films, cements, and in the recovery of acetic acid from aqueous solutions.

Acidity (as acetic)	0.02% by wt, max
Boiling point at 760 mm	88.6°C
Coefficient of expansion per °F	0.000727
Color	Water-white
Dilution ratios	
Toluene	2.7
V.M. and P. naphtha	0.92
Distillation range	84.5–90°C
Electrical conductivity at 25°C	5.7×10^{-7} recip ohms
Evaporation rate at 95°F (in minutes)	
5%	¼
25%	1¾
50%	4¼
75%	7½
90%	10¼
95%	11½
Flash point (Tag Closed Cup)	39°F
Freezing point	−73.4°C
Heat of vaporization	79.4 cal/gm
Non-volatile matter	2 mg per 100 cc, max
Refractive index, N 20/D	1.3772
Solubility of water in solvent	3.2% by wt
Specific gravity at 20/20°C	0.866 to 0.871
Specific heat at 15–25°C	0.521 cal/gm
Surface tension at 25°C	24.5 dynes/cm
Vapor pressure at 10°C	26.2 mm Hg
20°C	45.7 mm Hg
30°C	76.1 mm Hg
40°C	121.8 mm Hg
Viscosity at 20°C	0.00525 poises
Weight per gallon at 20°C	7.23 lbs

Constant Boiling Mixtures

			% by Wt	B.P. -C
Isopropyl Acetate	47.7	Isopropanol	52.3	80.1
Isopropyl Acetate	89.4	Water	10.6	76.6

***n*-Butyl Acetate** ($CH_3COOCH_2CH_2CH_2CH_3$). This ester is a water-white liquid with a characteristic fruity odor which is less pronounced than the odor of amyl acetate. It is miscible with alcohols, ketones, esters and most of the common organic solvents. It is a solvent for nitrocellulose and cellulose ethers especially when previously mixed with active or latent solvents. It will dissolve oils, fats, waxes, metallic resinates, camphor, cumar resins, dammar, ester gum, elemi, kauri, manila, mastic, pontianac, rosin, sandarac, chlorinated rubber, and such synthetic resins as the vinyls, polystyrene, and acrylates. In combination with 20 per cent of butyl alcohol, butyl acetate will dissolve the less highly polymerized alkyd resins, and shellac. Owing to its power of imparting low viscosity,

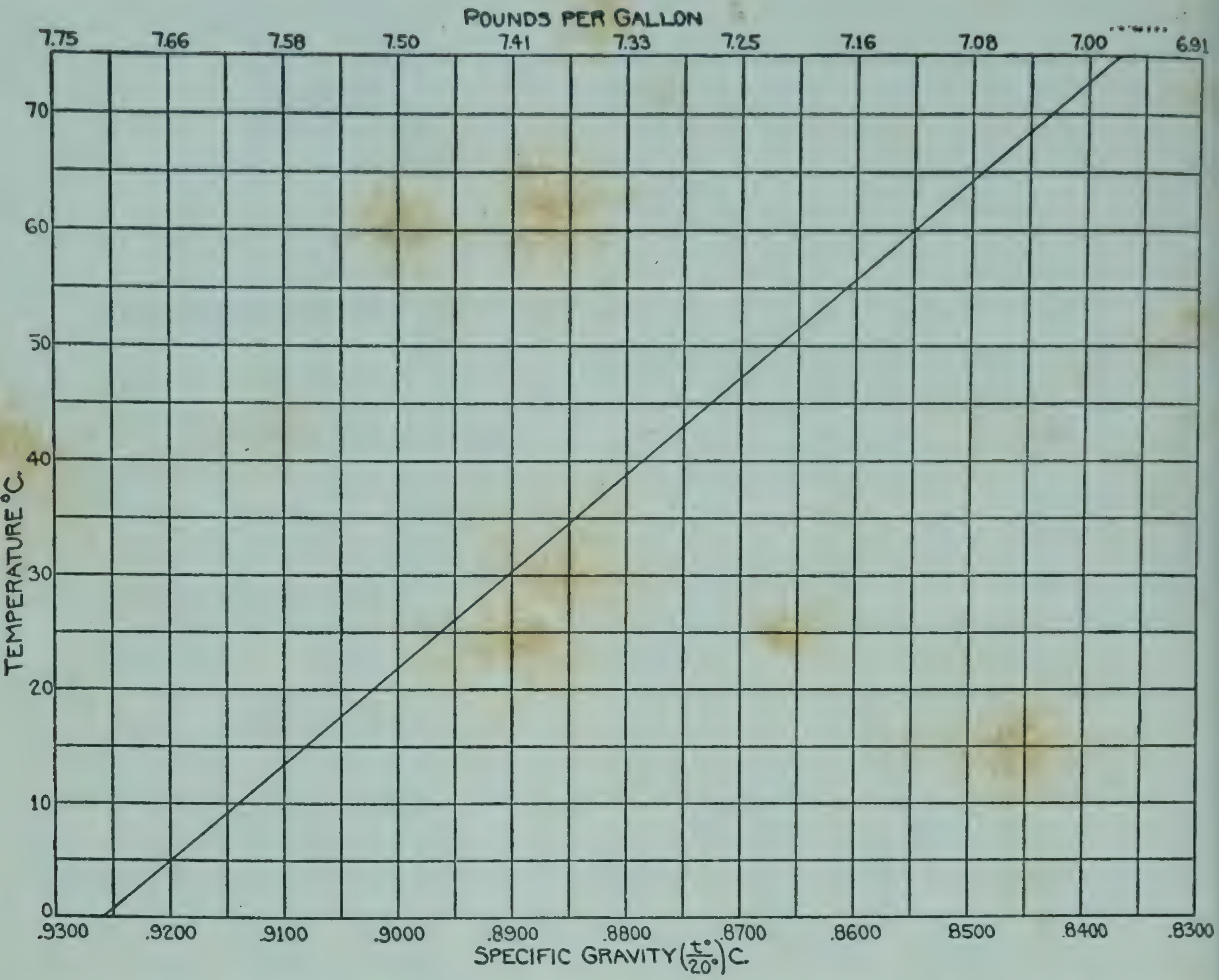


FIGURE 16.11. Specific Gravity and Weight per Gallon of Ethyl Acetate at Various Temperatures.[1]

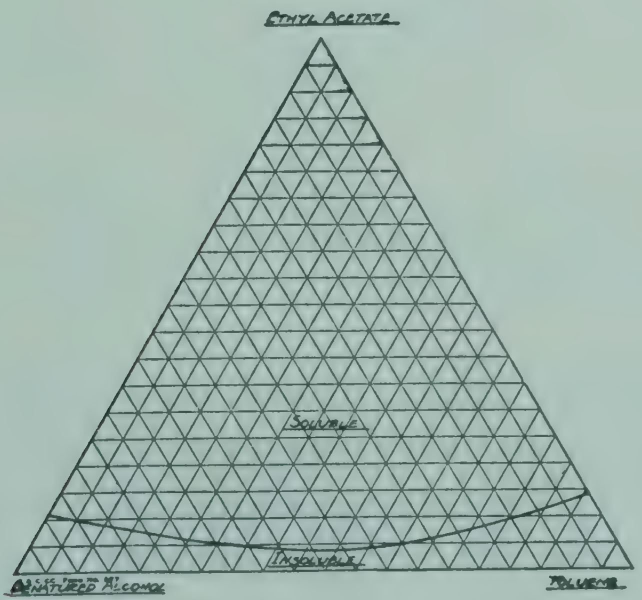


FIGURE 16.12.
Solubility of ½-Second R. S. Nitrocellulose in Mixtures of Ethyl Acetate, Denatured Alcohol, and Toluene.[1]

gum-compatibility, and good working qualities, it is classed among the best medium boiling solvents for nitrocellulose. Its volatility meets the demands of a lacquer solvent because it is sufficiently high to leave the film readily and at the same time low enough to prevent blushing. When combined with butyl alcohol it will prevent gum-blush, cotton-blush and chilling. As shown in the following wartime end-use pattern its largest use

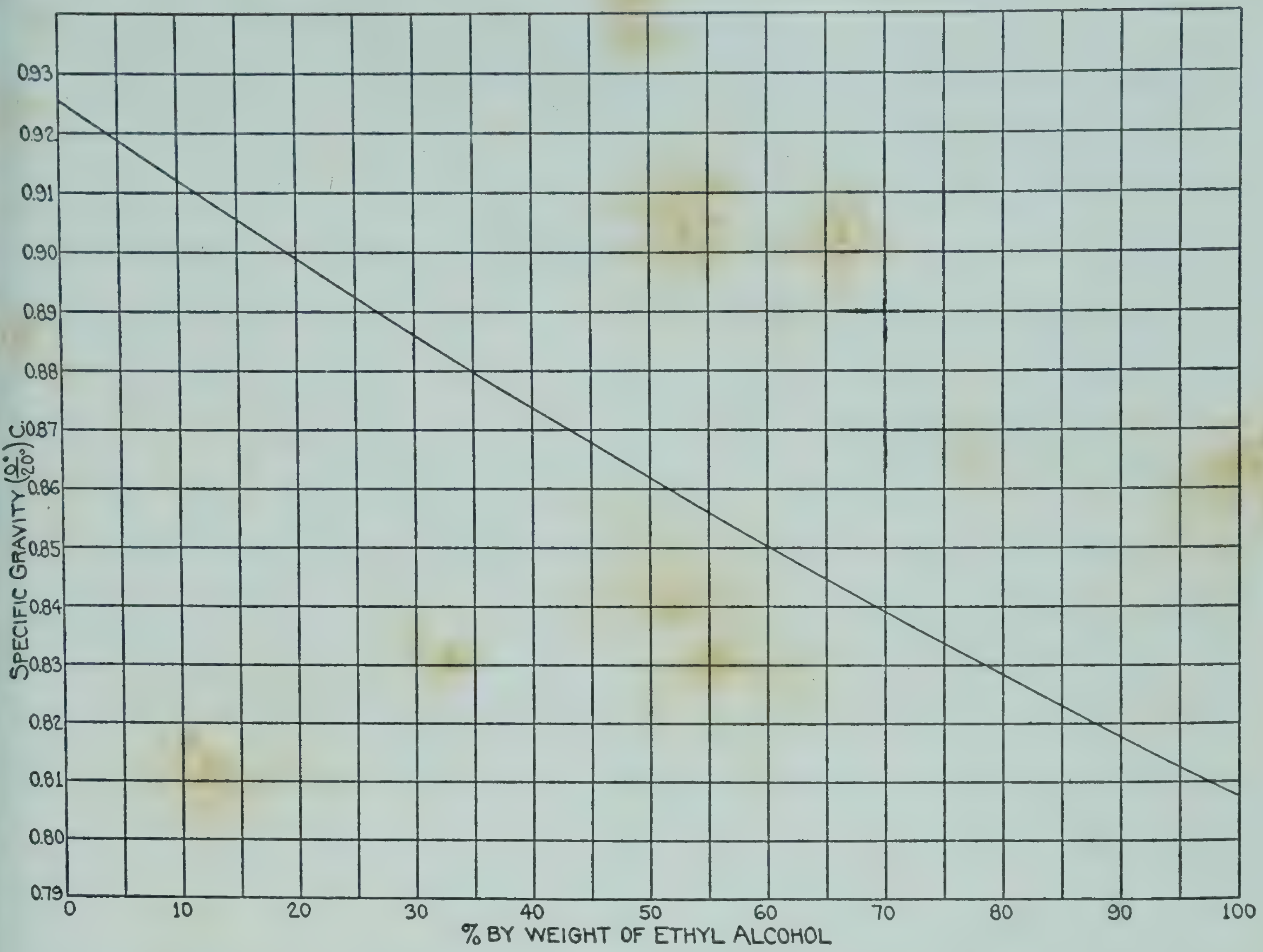


FIGURE 16.13. Specific Gravity of Ethyl Acetate-Ethyl Alcohol Mixtures at Room Temperature.[1]

is as a solvent in the manufacture of nitrocellulose lacquers for protective coatings, artificial leather and coated paper, plastics, polishes, safety glass, in perfumes, and flavoring materials.

ALLOCATIONS OF NORMAL BUTYL ACETATE: JULY 1, 1944–JUNE 30, 1945
(Thousands of pounds)

USE	TOTAL		JAN. 1–JUNE 30, 1945	JULY 1–DEC. 30, 1944
	Amount	Per cent		
Total Allocations	75,347	100.0	39,414	35,933
Export	9,309	12.4	2,681	6,628
Direct military[1]	7	[2]	7	0
Other uses	66,031	87.6	36,726	29,305
Protective coatings	63,467	84.2	35,291	28,176
De-icers	925	1.2	431	494
Cements and adhesives	617	0.8	431	186
Resins and plastics	201	0.3	90	111
Medicinals	133	0.2	99	34
Miscellaneous uses and small orders	688	0.9	384	304

[1] End-use data not available. [2] Less than one-tenth of one per cent.

	88–92%
Acidity (as acetic)	0.01% by wt, max
Boiling point at 760 mm Hg	126.5°C
Coefficient of cubical expansion (ordinary temperatures)	0.00067 per°F
	0.00121 per°C
Color	Water-white
Dielectric constant at 20°C	5.0
Dilution ratio	
Toluol	2.9
Petroleum naphtha	1.4
Distillation range	Below 115°C None
	Below 120°C Not more than 8%
	Above 130°C Not more than 5%
	Above 135°C None
Evaporation rate at 95°F (in minutes)	
5%	1¼
25%	6½
50%	13½
75%	22¾
90%	3¼
95%	34¾
Flash point	28°C
Heat of vaporization	73.8 calories per gm
Freezing point	−76.8°C
Non-volatile matter	0.005 gram per 100 cc, max
Residue	None
Refractive index at 20°C	1.3947
Solubility in water at 25°C	0.5% by vol
Solubility of water in solvent at 25°C	1.6% by vol
Specific gravity at 20/20°C	0.872 to 0.880
Vapor pressure at 0° C	3.0 mm Hg
25°C	15.0 mm Hg
50°C	45.0 mm Hg
Viscosity at 25°C	0.671 centipoises
Weight per gallon at 20°C	7.28 lbs

	98–100%
Acidity (as acetic)	0.01% by wt, max
Boiling point	126.5°C
Coefficient of expansion per 1°F	0006
per 1°C	0.0011
Color (A.P.H.A.)	10 max
Dilution ratio	
Toluol	3.05
Petroleum naphtha	1.40

Distillation range	123°–128°C
Electrical conductivity at 25°C	13×10^{-9} recip ohms
Flash point	82°F approx
Fractionation: I.P.	114.3°
10%	116.0
25%	116.9
50%	117.4
75%	117.6
90%	117.6
E.P.	118.1
Heat of vaporization	73.8 cal/gm
Non-volatile matter	Negligible
Refractive index at 20°C	1.3951
Solubility in water at 25°C	0.78% by wt
Solubility of water in solvent at 25°C	2.88% by wt
Specific gravity at 20/20°C	0.879 to 0.883
Specific heat at 21–27°C	0.505 cal/gm
Surface tension at 27°C	27.6 dynes/cm
Vapor pressure at 20°C	9.0 mm Hg
Viscosity at 25°C	0.00693 poises
Weight per gallon	7.76 lbs

Constant Boiling Mixtures

	% by Wt		% by Wt	B.P. °C
n-Butyl acetate	54.0	*n*-Butanol	46.0	118.0
n-Butyl acetate	60.0	*n*-Propanol	40.0	94.2
n-Butyl acetate	48.0	Isopropanol	52.0	80.1
n-Butyl acetate	71.3	Water	28.7	90.2

Ternary Mixtures

		B.P.
n-Butyl acetate	35.3%	89.4°C
n-Butanol	27.4%	
Water	37.3%	

sec-Butyl Acetate [$CH_3COOCH(CH_3)CH_2CH_3$]. sec-Butyl acetate is a colorless, flammable liquid with a fruity odor. It is miscible with castor and linseed oils and hydrocarbons, and will dissolve nitrocellulose, cumarone, elemi, ester gum, kauri, mastic, manila, pontianac, asphalt and tar. It has only partial solubility for dammar and shellac. Its solvency is very similar to *n*-butyl acetate but it has a lower boiling range, less blush resistance and will evaporate with greater rapidity. For this reason to replace *n*-butyl acetate it is necessary that this solvent should be mixed with slower evaporating solvents that can make up for its quicker rate of evaporation. It is largely used in the manufacture of nitrocellulose lacquers and similar types of coatings used in airplane dopes, artificial leather, celluloid products, coated paper, patent leather, and textile sizing and printing compounds.

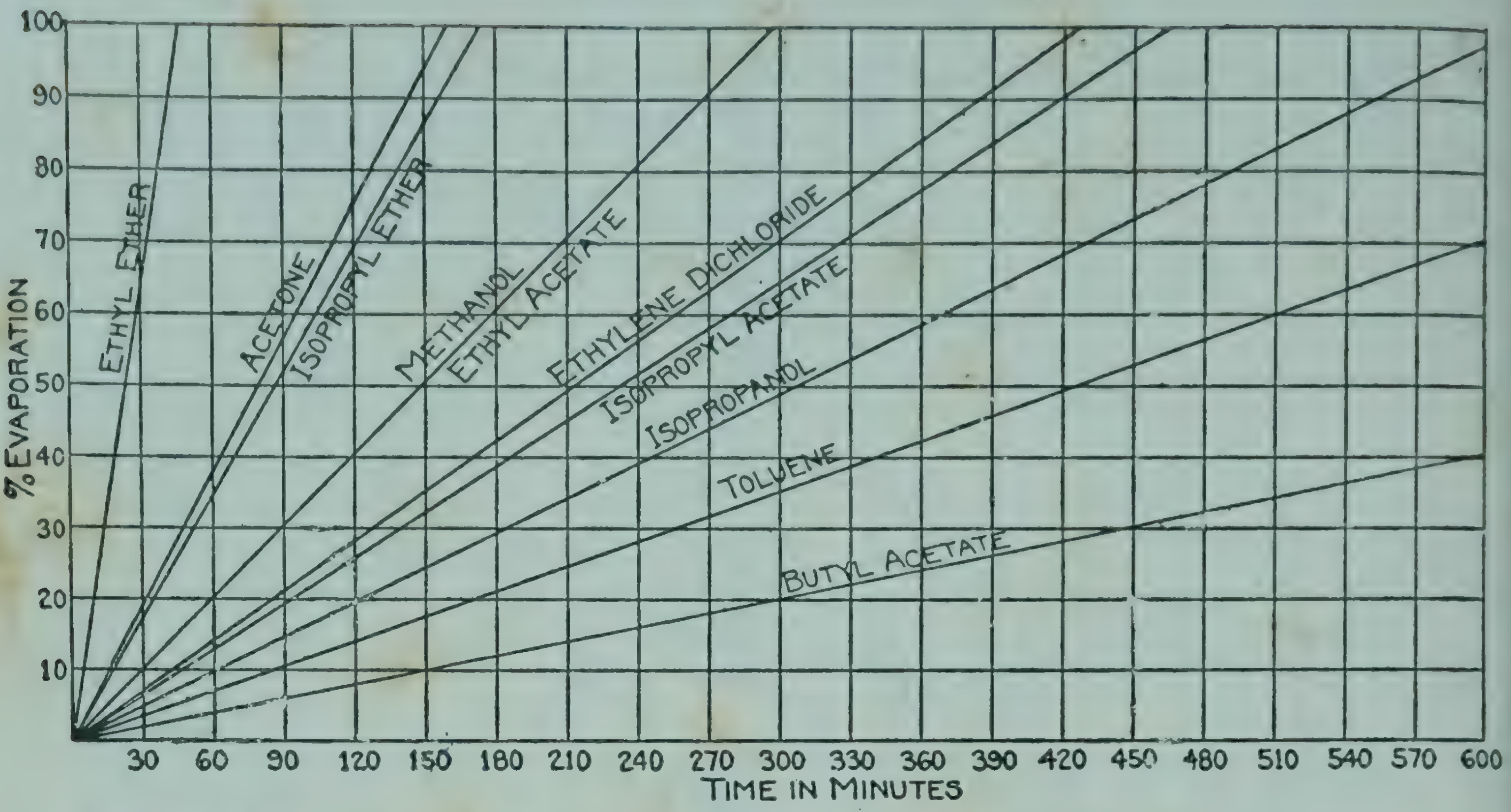


FIGURE 16.14. Evaporation Rate of Various Solvents at Room Temperature.[1]

Acidity (as acetic)	0.03% by wt, max
Blush resistance at 60°F	Clear 75% Relative humidity Blush 80%
Coefficient of expansion per 1°F	0.00063
per 1°C	0.00113
Color	Water-white
Distillation range:	
Below 104°C	None
Below 111°C	Not more than 10%
Below 114°C	Not more than 60%
Below 118°C	Not less than 90%
Above 130°C	None
Evaporation rate at 95°F (in minutes)	
5%	½
25%	3¾
50%	8½
75%	13½
90%	16¾
95%	18
Flash point	66°F
Non-volatile matter	0.005 gm per 100 cc, max
Residue	None
Refractive index, N 25.3/D	1.3866
Specific gravity at 20/20°C	0.862–0.866
Solubility in water	0.74% by wt
Solubility of water in solvent at 25°C	2.1% by wt
Weight per gal at 20°C	7.19 lbs (approx.)

	88–92%
Acidity (as acetic)	0.02% by wt, max
Boiling point at 760 mm	112.4°C
Coefficient of expansion per °F	0.000668
Distillation range (ASTM)	
I.B.P.	Not less than 104°C
10%	Not less than 108°C
50%	Not less than 110°C
90%	Not more than 110°C
Dry Point	Not more than 125°C
Flash point (Tag Closed Cup)	64°F
Heat of vaporization	74.7 cal/gm
Non-volatile matter	2 mg per 100 ml, max
Refractive index, N 20/D	1.3887
Specific gravity at 20/20°C	0.860 to 0.866
Vapor pressure at 10°C	8.9 mm Hg
20°C	16.2 mm Hg
30°C	28.3 mm Hg
40°C	47.4 mm Hg
Weight per gal at 20°C	7.18 lbs

Azeotropic Mixtures

				B.P.
sec-Butyl acetate	77.5%	Water	22.5%	87.0°C
sec-Butyl acetate	13.7%	sec-Butanol	86.3%	99.6°C

Isobutyl Acetate [$CH_3COOCH_2CH(CH_3)_2$]. Isobutyl acetate is a colorless liquid with a mild and pleasant odor. Commerical grade isobutyl acetate has an ester content of 88 to 92 per cent, the balance being substantially isobutyl alcohol. The solvent power of this ester is similar to that of the normal and secondary acetates. It is miscible with most organic solvents and will dissolve a large number of oils, waxes, and natural and synthetic resins.

Acidity (as acetic)	0.03% by wt, max
Distillation range at 760 mm	107°–125°C
Color	Water-white
Water	Miscible with 19 vols 60° Bé gasoline
Flash point	25°C (77°F)
Refractive index at 25°C	1.388
Solubility in water at 20°C	2% by vol
Solubility of water in solvent at 20°C	2.7% by vol
Specific gravity at 20/20°C	0.863–0.868
Weight per gal at 20°C	7.20 lbs

Amyl Acetate (Banana oil, Amyl acetic ether, Isoamyl acetate) $CH_3COOC_5H_{11}$. Amyl acetate is a colorless, flammable liquid with an odor resembling bananas or pears. Its exceptional solvent power places it

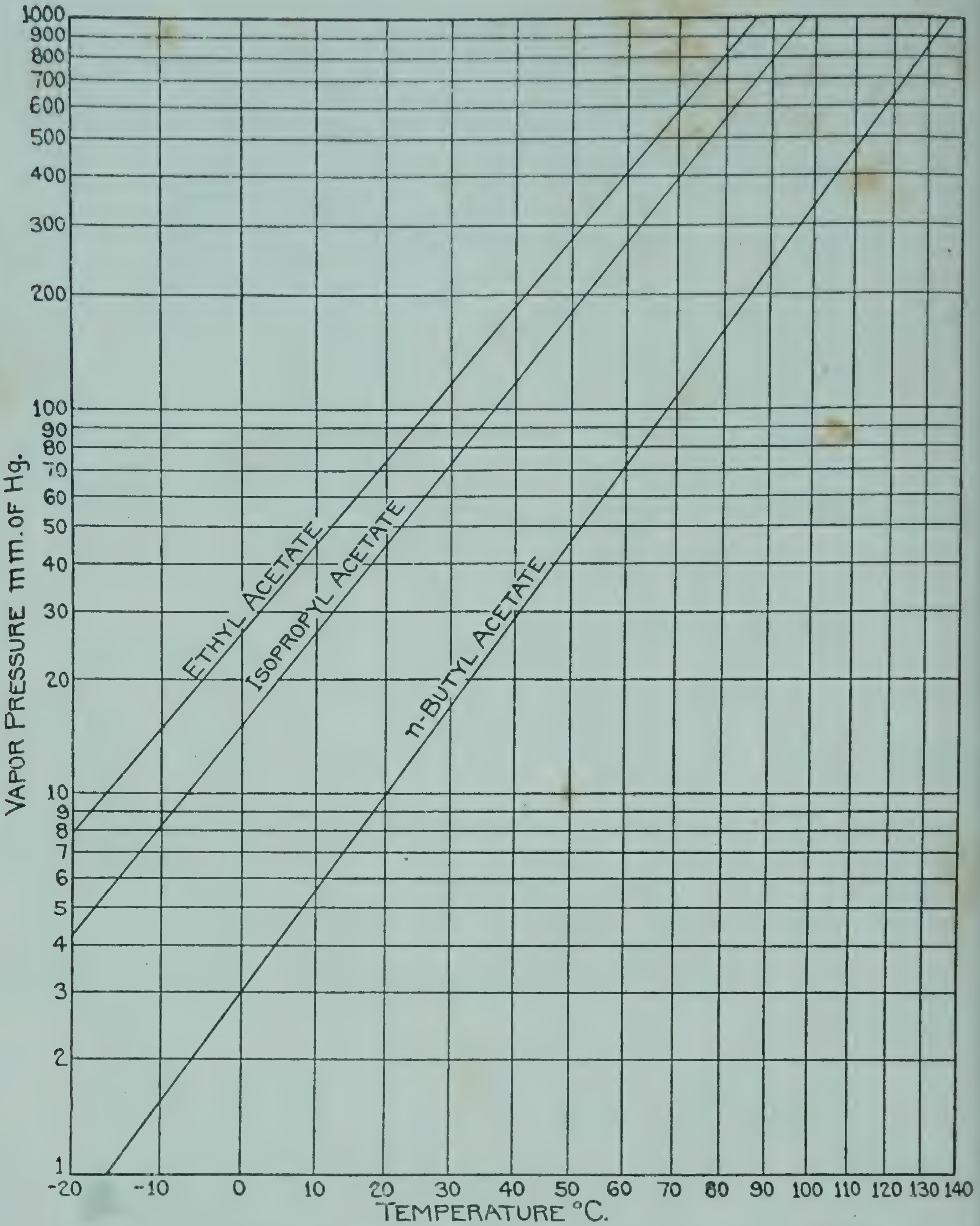


Figure 16.15. Vapor Pressure of Some Esters at Various Temperatures.[1]

among the first solvents in the nitrocellulose lacquer industry. The amyl acetates are made by the acetylation of fusel oil or synthetic amylalcohols. Amyl acetate is miscible with oils, hydrocarbons, alcohols, ethers and esters, and will dissolve such substances as camphor, elemi, ester gums, copal ester, copals, dammar, kauri, rosin, sandarac, tannins, waxes, zanzibar and cumar resins, and, when it is mixed with alcohol it will dissolve some alkyd resins. It is a good solvent for cellulose esters and ethers, the

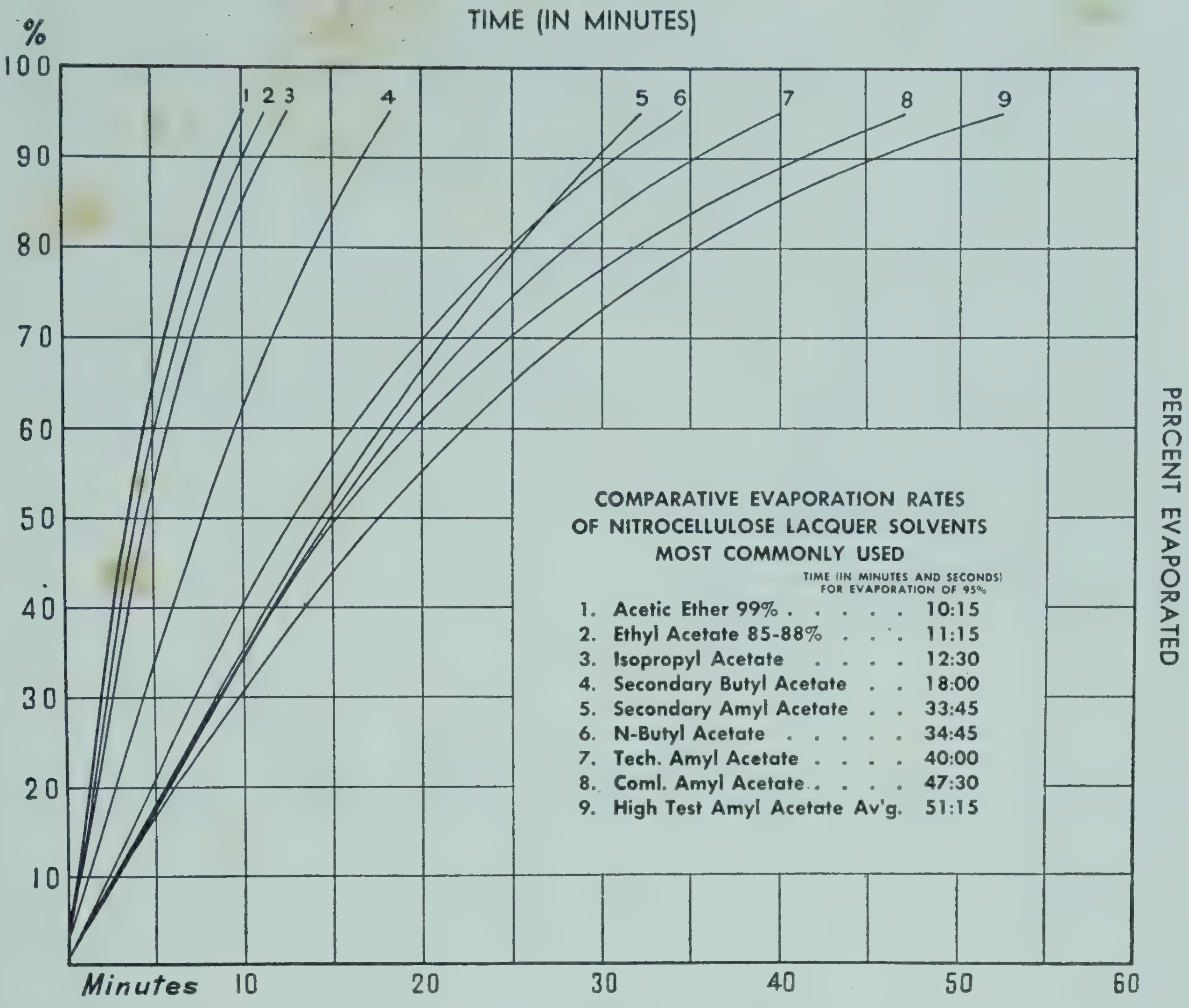


FIGURE 16.16. Comparative Evaporation Rates.

solvency of which is increased when combined with ethyl alcohol. Amyl acetate is used extensively as a solvent in nitrocellulose lacquers, both for its solvency and its power to impart blush resistance, good flow, gloss and toughness. It is also used in making smokeless powder, artificial leather and pearls, airplane dopes, waterproofing compositions, varnishes, dry cleaning compounds, bronzing liquid, films, celluloid, rayon, linoleum, oil-cloth, fruit flavors, soft drinks, food preparations, confectionery, perfumes, soap solvent, and in photoengraving.

85–88% technical grade

Acidity (as acetic)	0.03% by wt, max
Blush resistance at 90°F (10% ½ sec R.S. nitrocellulose solution)	Clear 80% Relative humidity Blush 85%
Coefficient of expansion per 1°F	0.00066
per 1°C	0.00119
Color	Water-white
Dilution ratio	
Toluol	2.7
Petroleum naphtha	1.4
Distillation range	
Below 110°C	Not more than 15%
Below 120°C	Not more than 30%

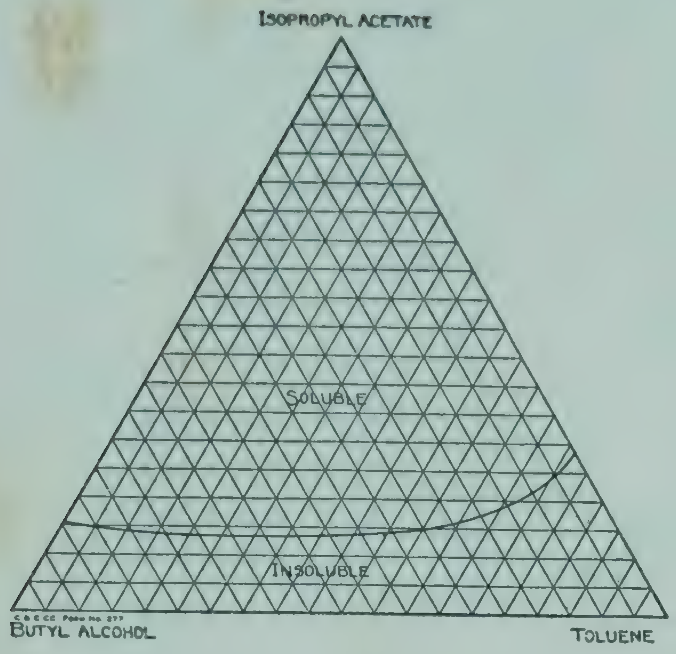


FIGURE 16.17.
Solubility of ½-Second R. S. Nitrocellulose in Mixtures of Isopropyl Acetate, Butyl Alcohol, and Toluene.[1]

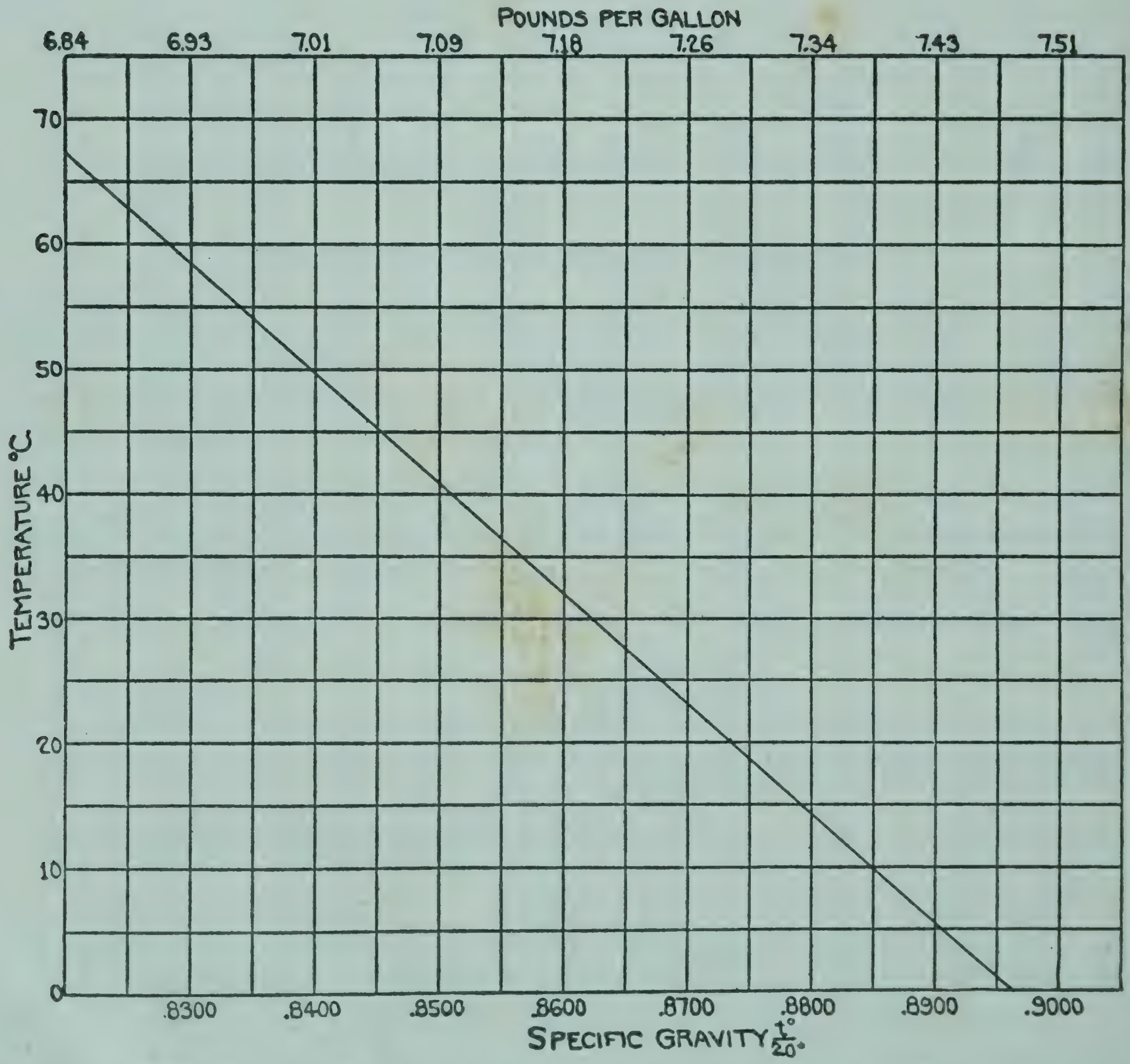


FIGURE 16.18. Specific Gravity of Isopropyl Acetate at Various Temperatures.[1]

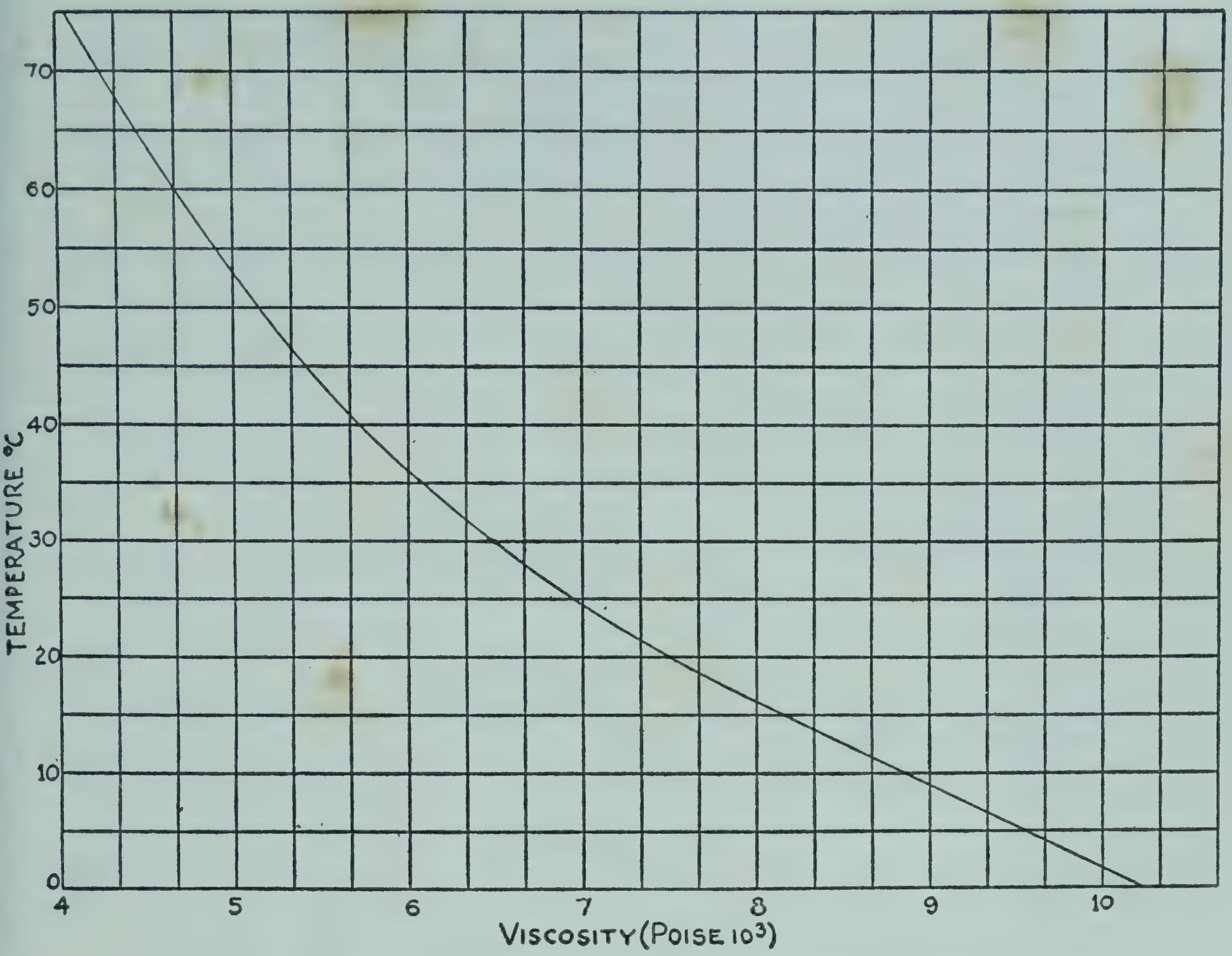


FIGURE 16.19. Viscosity of Isopropyl Acetate at Various Temperatures.[1]

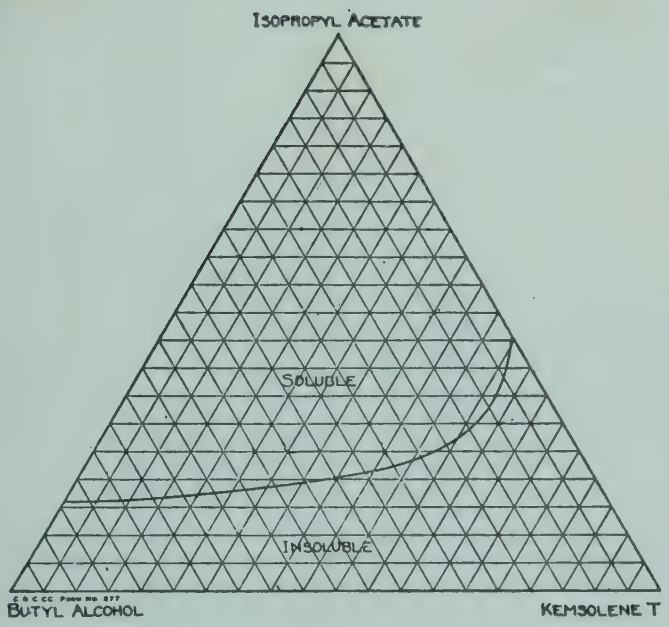


FIGURE 16.20. Solubility of $\frac{1}{2}$-Second R. S. Nitrocellulose in Mixtures of Isopropyl Acetate, Isopropyl Alcohol, and Kemsolene T.[1]

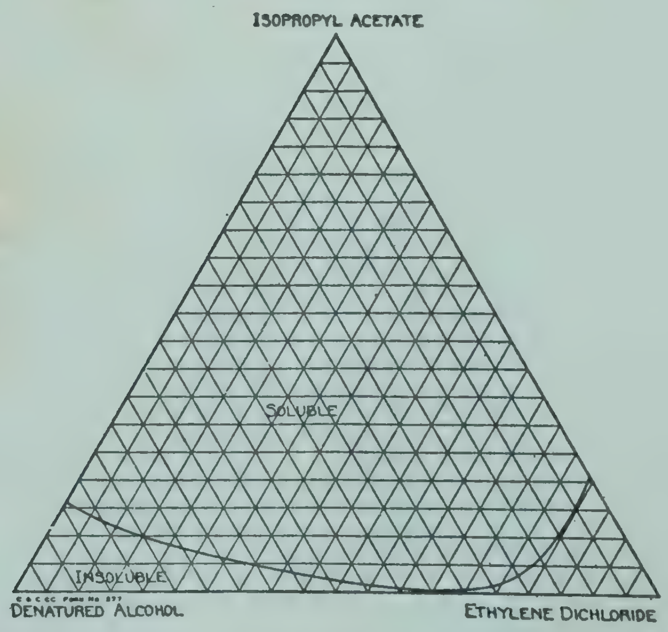


FIGURE 16.21. Solubility of $\frac{1}{2}$-Second R. S. Nitrocellulose in Mixtures of Isopropyl Acetate, Denatured Alcohol, and Ethylene Dichloride.[1]

Below 130°C	Not more than 55%
Below 140°C	Not less than 80%
Above 150°C	None
Dryness	Miscible without turbidity with 20 vols 60° Bé gasoline at 20°C
Evaporation rate at 95°F (in minutes)	
5%	1
25%	6
50%	15¼
75%	28½
90%	41¼
95%	47½
Flash point	63°F
Non-volatile matter	0.005 gm per 100 cc, max
Solubility of water in solvent at 25°C	2.4% by vol
Specific gravity at 20/20°C	0.857–0.865
Viscosity (10% ½ sec. R.S. nitrocellulose solution)	43 centipoises
Weight per gal at 20°C	7.17 lbs

(High Test 85–88%)

Acidity (as acetic)	Not more than 0.03%
Blush resistance at 90°F (10% ½ sec. R.S. nitrocellulose solution)	Clear 85% Relative humidity Blush 90%
Coefficient of expansion per 1°F	0.00066
per 1°C	0.00119
Color	Water-white
Dilution ratio	
Toluol	2.5
Petroleum naphtha	1.4
Distillation range	
Below 110°C	None
Below 120°C	Not more than 10%
Below 130°C	Not more than 40%
Below 140°C	Not less than 60%
Below 150°C	None
Evaporation rate at 95°F (in minutes)	
5%	1½
25%	8¼
50%	18½
75%	30
90%	45
95%	51¾
Flash point	84°F

Non-volatile matter	Not more than 0.005 gm per 100 cc
Odor	Mild
Odor residual	Non-residual
Purity	Ester content as amyl acetate 85–88%
Solubility of water in solvent at 25°C	100 cc solvent dissolves 1.8 cc water
Specific gravity at 20/20°C	0.859–0.863
Viscosity (10% ½ sec. R.S. nitrocellulose solution)	61 centipoises
Weight per gal at 20° C	7.17 lbs

90–95% grade

Acidity (as acetic)	0.035% by wt, max
Blush resistance at 90°F (10% ½ sec. R.S. nitrocellulose solution)	Clear 85% Relative humidity Blush 90%
Coefficient of expansion	
per 1°F	0.00061
per 1°C	0.00110
Color	Water-white
Dilution ratio	
Toluol	2.6
Petroleum naphtha	1.4
Evaporation rate at 95°F (in minutes)	
5%	1¼
25%	7
50%	15½
75%	25¾
90%	35
95%	40
Flash point	79°F
Distillation range	
Below 110°C	None
Below 120°C	Not more than 10%
Below 130°C	Not more than 70%
Below 140°C	Not less than 90%
Above 150°C	None
Non-volatile matter	0.005 gram per 100 cc, max
Residue	None
Solubility in water at 25°C	2% by vol
Solubility of water in solvent at 25°C	2% by vol
Specific gravity at 20/20°C	0.868 to 0.872
Viscosity (10% ½ sec. R.S. nitrocellulose solution)	60 centipoises
Weight per gal at 20°C	7.22 lbs

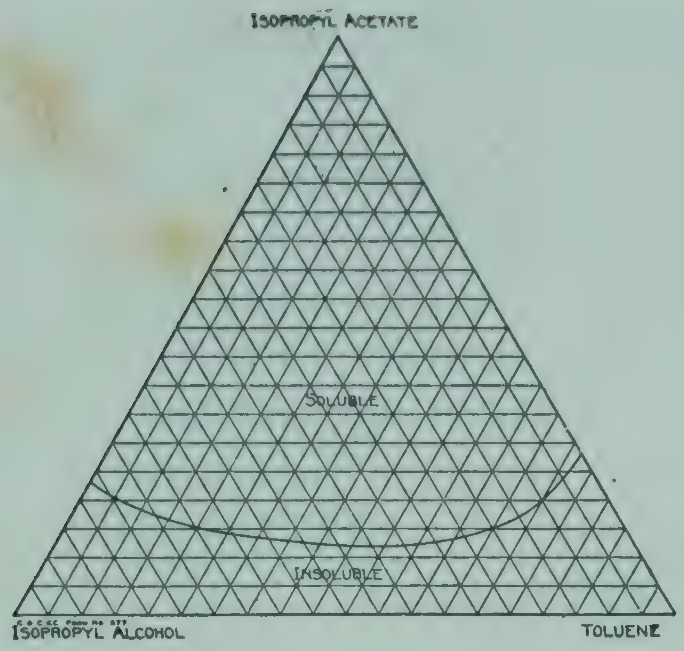


Figure 16.22. Solubility of ½-Second R. S. Nitrocellulose in Mixtures of Isopropyl Acetate, Isopropyl Alcohol, and Toluene.[1]

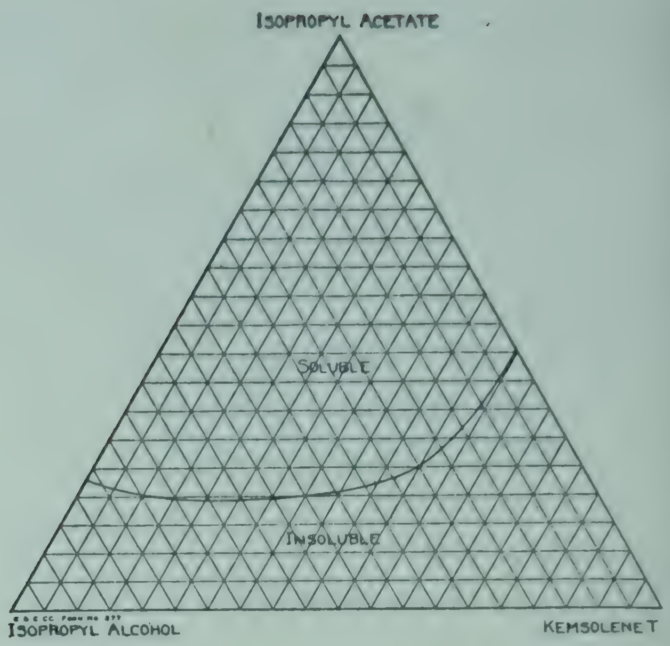


Figure 16.23. Solubility of ½-Second R. S. Nitrocellulose in Mixtures of Isopropyl Acetate, Butyl Alcohol, and Kemsolene T.[1]

sec-Amyl Acetate ($CH_3COOC_5H_{11}$). This medium boiling solvent is a water-white liquid made by acetylation from the secondary amyl alcohols (pentanol-2 and pentanol-3). Although its solvent power is not equal to that of amyl acetate because it has a lower tolerance for diluents, as well as a less desirable odor, it has many similar properties and it is used as a nitrocellulose and ethyl cellulose solvent.

Acidity (as acetic)	0.03% by wt, max
Blush resistance at 90°F (10% ½ sec. R.S. nitrocellulose solution)	Clear 85% Relative humidity Blush 90%
Coefficient of Expansion	
per 1°F	0.00060
per 1°C	0.00108
Color	Water-white
Dilution ratio	
Toluol	2.1
Petroleum naphtha	1.1
Distillation range	
Below 123°C	None
Below 126°C	Not more than 10%
Below 132°C	Not more than 60%
Below 140°C	Not less than 90%
Above 145°C	None
Evaporation rate at 95°F (in minutes)	
5%	1½
25%	7½
50%	15½
75%	24½
90%	30½
95%	33¾

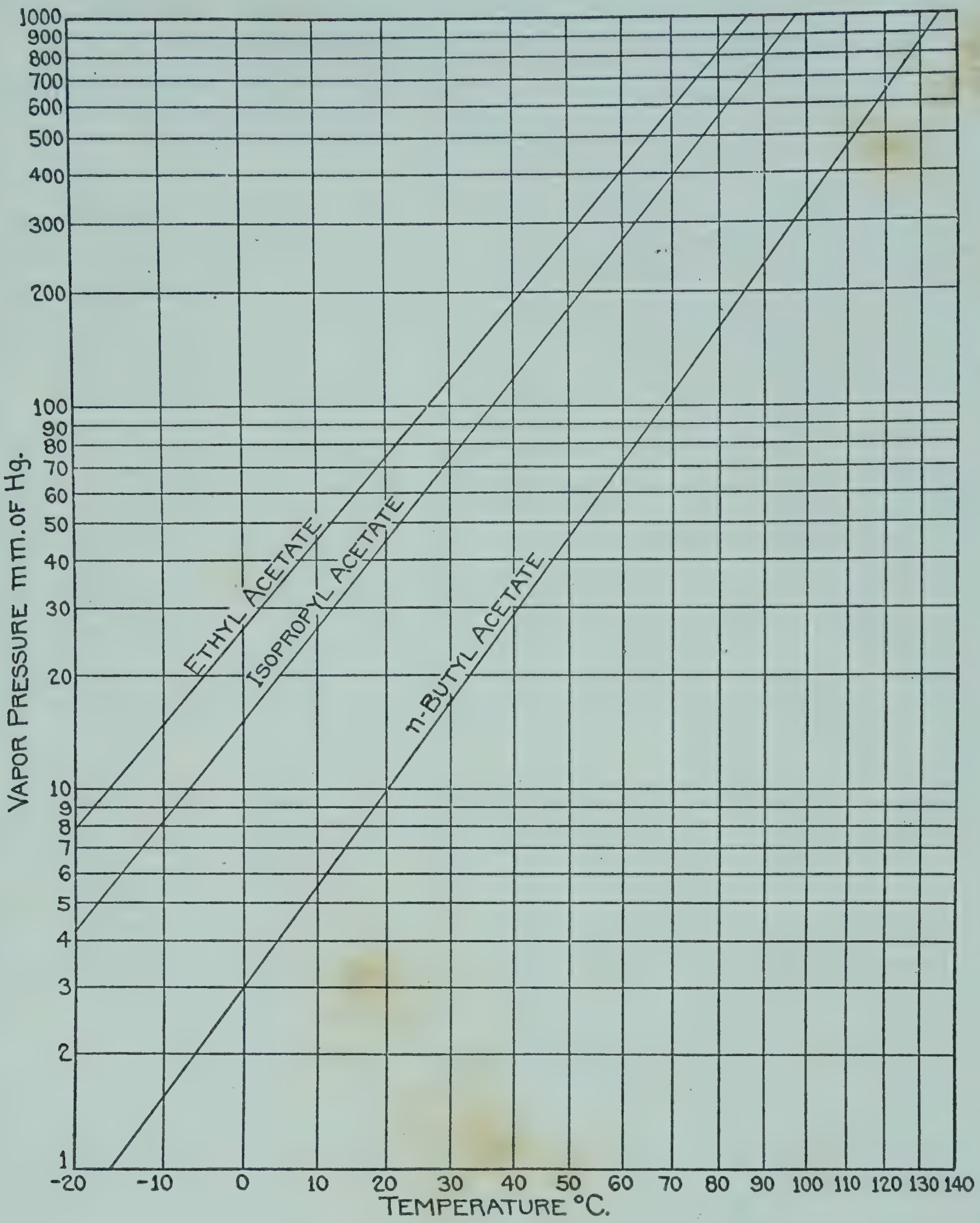


FIGURE 16.24. Vapor Pressure of Esters.

Flash point	89° F
Non-volatile matter	0.005 gm per 100 cc, max
Residue	None
Specific gravity at 20/20°C	0.862–0.866
Solubility of water in solvent at 25°C	0.8% by vol
Viscosity (10% $\frac{1}{2}$ sec. R.S. nitrocellulose solution)	75 centipoises
Weight per gal at 20°C	7.19 lbs

TABLE 16.1.—RELATIVE RATES OF EVAPORATION OF ACTIVE SOLVENTS, LATENT SOLVENTS, DILUENTS AND SOLVENT COMBINATIONS[2]

ACTIVE SOLVENTS	RELATIVE RATE OF EVAPORATION (Normal Butyl Acetate = 1.0)
Acetone	7.7
Methyl Ethyl Ketone	4.6
Commercial Ethyl Acetate	4.2
Isopropyl Acetate	3.1
Methyl Normal Propyl Ketone	2.0
Secondary Butyl Acetate	1.8
Methyl Isobutyl Ketone	1.6
Nitromethane	1.3
Nitroethane	1.2
2-Nitropropane	1.1
Normal Butyl Acetate	1.0
Methyl Normal Butyl Ketone	1.0
Mesityl Oxide	0.9
Secondary Amyl Acetate	0.8
1-Nitropropane	0.7
Pentacetate	0.6
Methyl Amyl Acetate	0.5
Methyl Normal Amyl Ketone	0.4
Diisobutyl Ketone	0.3
Cellosolve	0.2
Cellosolve Acetate	0.2
Diacetone Alcohol	0.2
Ethyl Lactate	0.2
Butyl Cellosolve	0.1
Normal Butyl Lactate	<0.1
Isophorone	<0.1
LATENT SOLVENTS	
Ethyl Alcohol, anhydrous	1.9
Isopropyl Alcohol, 99%	1.7
Ethyl Alcohol, 190 proof	1.7
Secondary Butyl Alcohol	1.0
Normal Butyl Alcohol	0.5
Secondary Amyl Alcohol	0.5
Pentasol	0.3
Methyl Isobutyl Carbinol	0.3

Pentacetate. Pentacetate made from synthetic amyl alcohol, is a mixture of five isomeric amyl acetates with some free amyl alcohol. It is soluble in methanol, ethyl ether, ethyl acetate, fixed oils, acetone, oleic acid, hot stearic acid, and aromatic and aliphatic hydrocarbons. It is soluble in hot paraffin and carnauba waxes but these congeal on cooling. It is insoluble

TABLE 16.2.—DILUTION RATIOS WITH NITROCELLULOSE*

SOLVENT	DILUENT MIXTURE[3]					
	% Butanol 0 % Toluene 100	20 80	40 60	60 40	80 20	100 0
Ethyl lactate	6.0	18.0	30.0	35.0	27.0	22.5
"Cellosolve"	6.0	11.0	19.0	15.0	11.0	9.5
"Cellosolve" acetate	2.5	8.5	22.0	18.0	12.5	8.5
Butyl propionate	2.0	7.5	16.0	17.5	16.0	14.0
Amyl acetate	2.0	5.0	10.0	18.0	15.5	14.0
Butyl "Cellosolve"	5.2	7.4	11.6	8.5	6.0	5.8
	DILUENT MIXTURE[3]					
	% Butanol 0 % Dryolin 100	20 80	40 60	60 40	80 20	100 0
Ethyl lactate	0.5	2.3	7.0	10.8	15.5	22.5
"Cellosolve"	1.0	2.0	4.2	5.4	7.2	9.5
"Cellosolve" acetate	0.8	1.7	3.2	5.0	7.0	8.5
Butyl propionate	1.0	3.0	3.8	6.0	9.5	14.0
Amyl acetate	1.5	2.6	4.8	6.6	10.0	14.0
Butyl "Cellosolve"	2.0	2.1	2.1	3.8	4.2	5.8
Lacquer Thinners[3]						
Ethyl lactate	10	5	5	5	5	5% (by vol.)
Ethyl acetate	10	15	10	8	20	—
Butyl acetate	—	—	15	6	—	15
Butyl alcohol	10	5	10	10	5	15
Toluene	70	75	—	30	50	—
Petroleum	—	—	60	41	20	65
Mist Coats[3]						
Ethyl lactate	15	15	10	15	10	15% (by vol.)
Di-acetone alcohol	—	10	—	10	10	—
Butyl acetate	—	—	10	—	5	10
Butyl alcohol	—	—	10	10	10	10
Toluene	85	75	—	—	—	—
Petroleum	—	—	70	65	65	65

* Two-gram portions of $\frac{1}{2}$-sec. nitrocellulose (dry) were dissolved in 20 cc of the solvent, and diluted until nitrocellulose was precipitated.

in water. The solvent power of this mixture being similar to that of amyl acetate Pentacetate finds its most important use in the manufacture of nitrocellulose lacquers. It is also used as an extractant in the production of penicillin.

It also finds use in various types of poison bait.

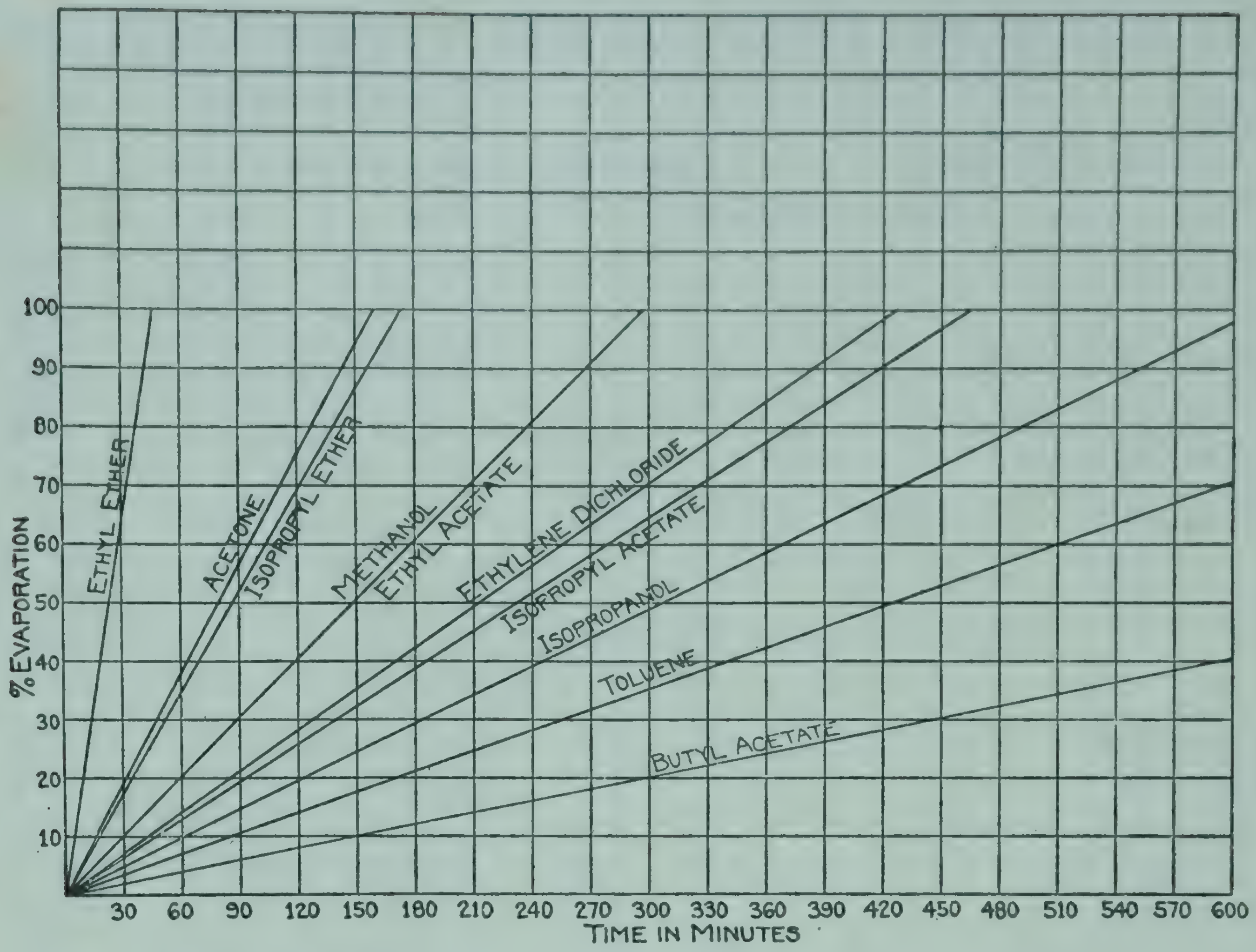


FIGURE 16.25. Comparative Rates of Evaporation.

Some of the esters to be found in Pentacetate are:

	B.P.
$CH_3CH_2CH_2CH_2CH_2OOCCH_3$	148°C
$(CH_3)_2CHCH_2CH_2OOCCH_3$	142°C
$CH_3CH_2CH(CH_3)CH_2OOCCH_3$	142°C
$CH_3CH(OOCCH_3)CH_2CH_2CH_3$	134°C
$CH_3CH_2CH(OOCCH_3)CH_2CH_3$	132°C

Acidity (as acetic)	0.03% by wt max
Coefficient of expansion at 10 to 35°C	0.00110 per °C
Color	Water-white
Distillation range	
100%	Above 126°C
95%	Above 130°C
75%	Above 135°C
25%	Above 140°C
End point	Not above 150°C
Dilution ratio	
Toluol	2.1
Petroleum naphtha	1.3
Evaporation rate at 114.8°F	
Minutes 3.92	25%
Minutes 7.92	50%
Minutes 12.50	75%
Minutes 20.00	100%

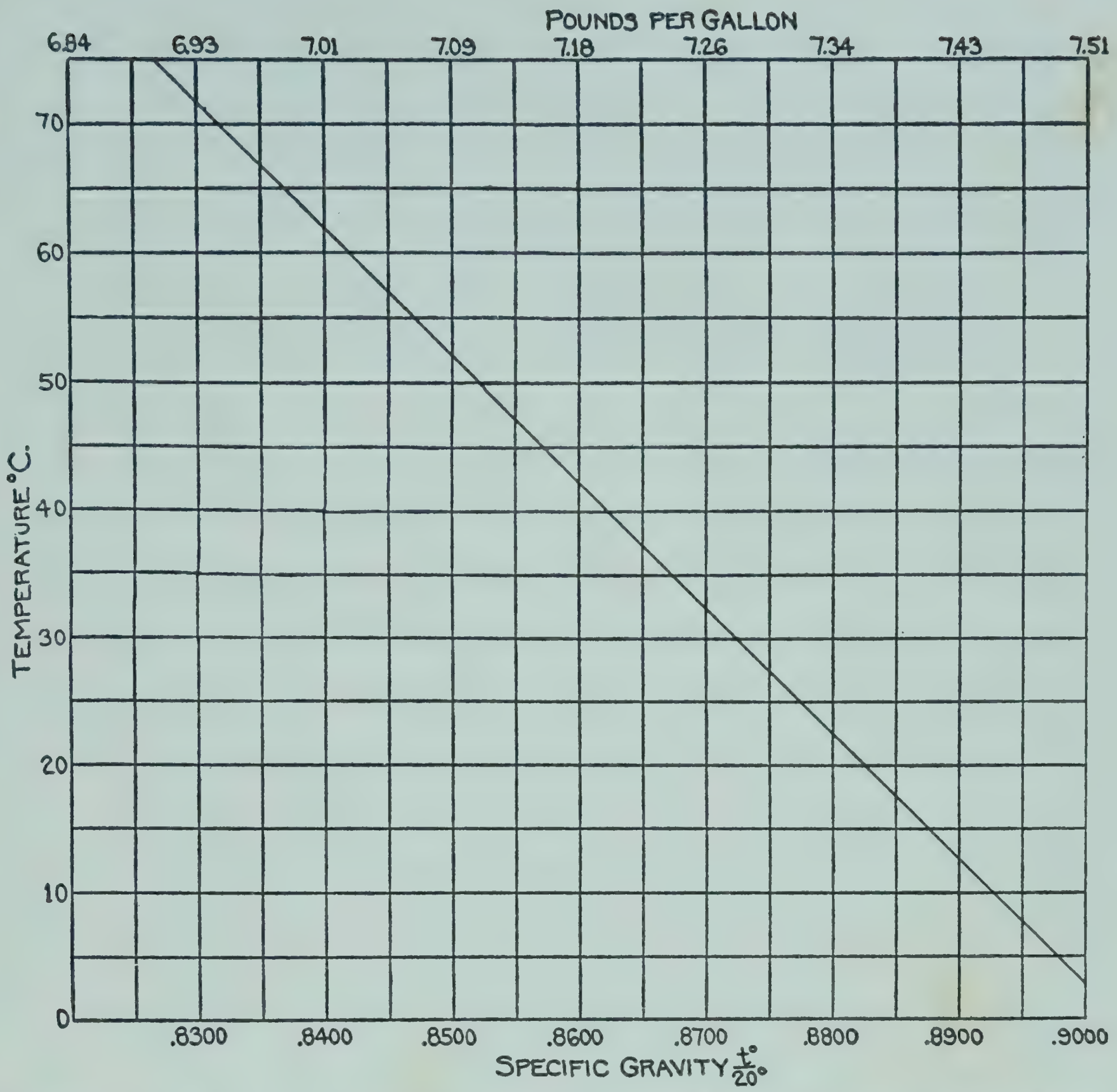


FIGURE 16.26. Specific Gravity of Butyl Acetate at Various Temperatures.[1]

Flash point (Open Cup)	107°F
Heat of vaporization	68.5 cal/gm
Non-volatile	0.005 gm/100 cc max
Refractive index at 20°C	1.4013
Specific gravity at 20/20°C	0.860–0.870
Solubility in water	1% by vol
Solubility of water in solvent	1.5% by vol
Viscosity at +40°C	0.683 centipoises
−40°C	3.464 centipoises
Water azeotropic mixture at 92–95°C	67% Pentacetate (approx) 33% water by vol
Water content	None
Weight per gal	7.21 lbs

The viscosity of solutions of 32 oz. of cotton to one gallon of solvent is given in Table 16.3 in relative figures for comparison.

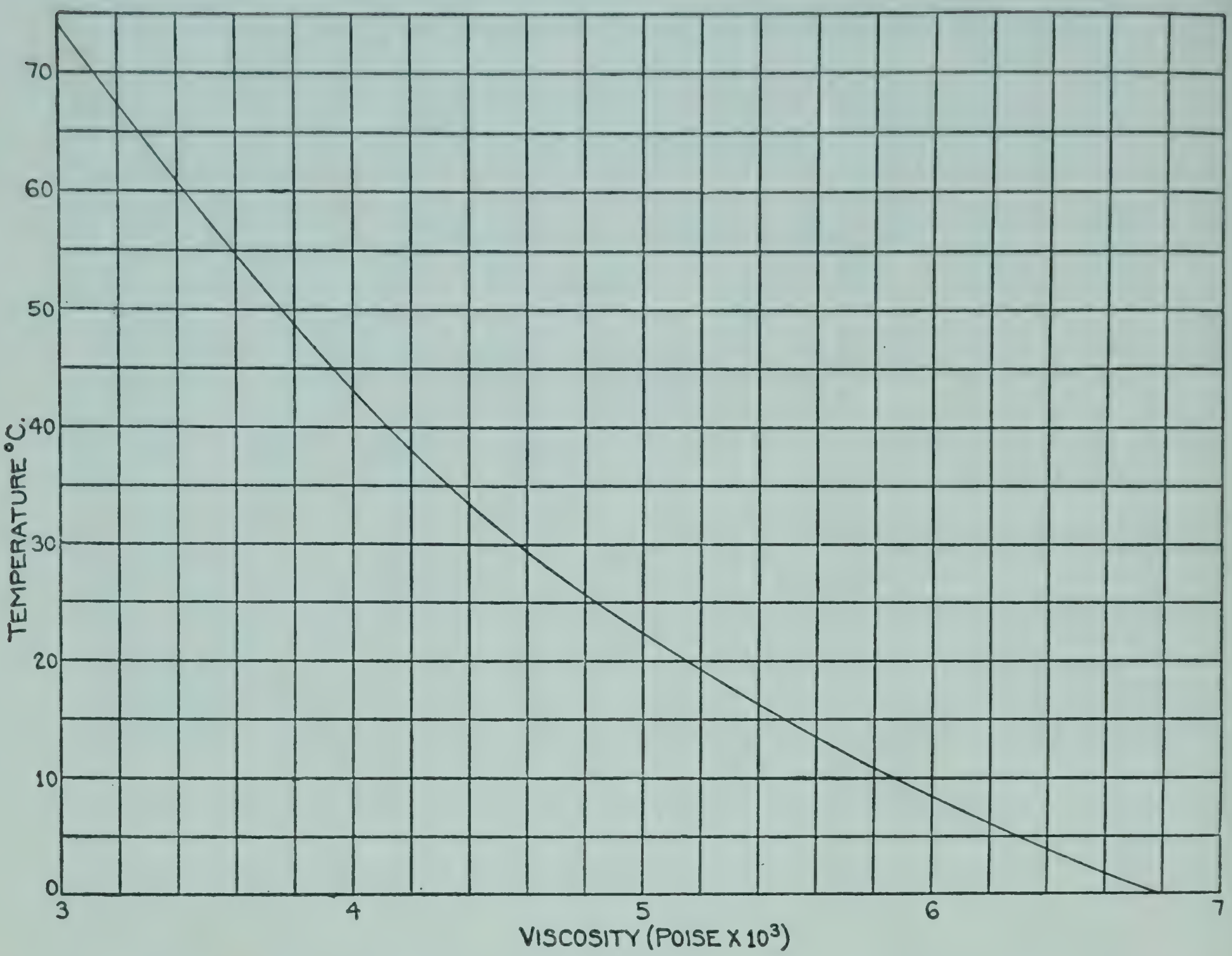


FIGURE 16.27. Viscosity of n-Butyl Acetate at Various Temperatures.[1]

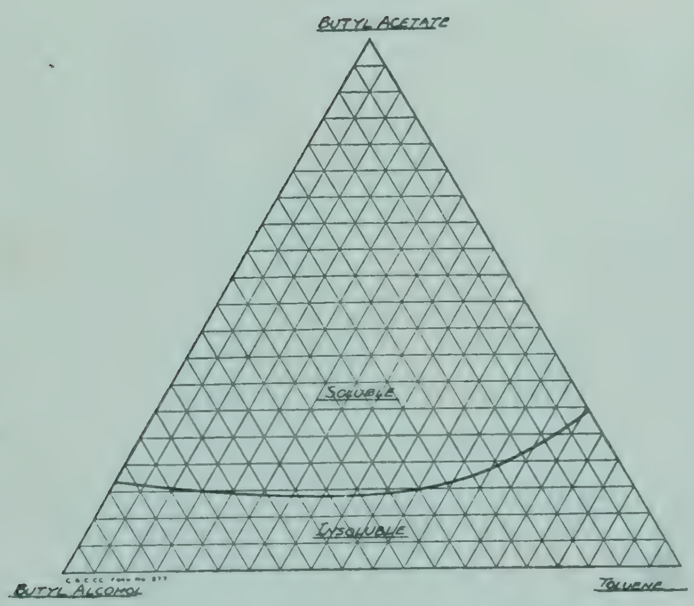


FIGURE 16.28. Solubility of ½-Second R. S. Nitrocellulose in Mixtures of Butyl Acetate, Butyl Alcohol, and Toluene.[1]

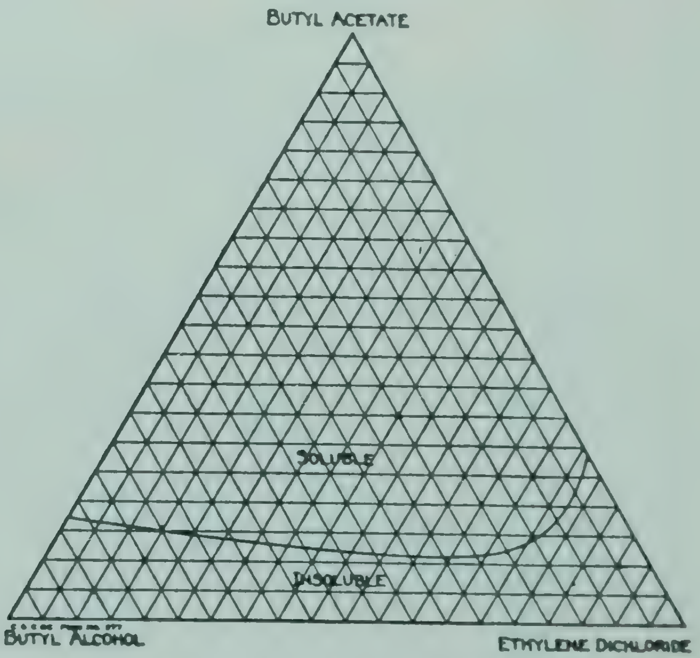


FIGURE 16.29. Solubility of ½-Second R. S. Nitrocellulose in Mixtures of Butyl Acetate, Butyl Alcohol, and Ethylene Dichloride.

	SOLVENTS[2]	MOLECULAR WEIGHT	PURITY OF COMMERCIAL PRODUCT	SPECIFIC GRAVITY RANGE 20°/20°C	POUNDS PER GALLON (APPROX.), 20°C	BOILING RANGE, °C (760 MM)	FREEZING POINT, °C	VAPOR PRESSURE, MM Hg, 20°C	FLASH POINT, OPEN CUP, °F	SURFACE TENSION, DYNES/CM	SOLUBILITY OF COMPOUND IN WATER, % BY WEIGHT	SOLUBILITY OF WATER IN COMPOUND, % BY WEIGHT	AZEOTROPE WITH WATER		RELATIVE RATE OF EVAPORATION (n-BuOAc = 1)	DILUTION RATIO			VISCOSITY OF 8% RS ½" NITROCELLULOSE SOLUTION, HERCULES CAPILLARY TUBE, 25°C (CENTIPOISES)	BLUSH RESISTANCE	
													Boiling Point, °C	Weight Per Cent of Compound		Toluene	Aromatic Petroleum Naphtha	Aliphatic Petroleum Naphtha			
1	Ethyl Acetate	88.10	97%	0.894–0.900	7.46	73–86	−82.4	73	40	—	7.9	3.0	70.4	93.0	4.1	2.7	1.4	1.0	20	50	1
2			85%	0.882–0.888	7.37	70–85				22.9					4.2	3.1	1.6	1.0	15	38	2
3	Isopropyl Acetate	102.13	95%	0.866–0.871	7.23	84.5–90	−73.4	47.5	54	21.2	2.9	2.0	76.6	89.4	3.1	2.6	1.4	1.0	20	63	3
4			85%	0.860–0.870	7.18	81–95									3.0	2.9	1.7	1.2	22	62	4
5	n-Butyl Acetate	116.16	90%	0.872–0.880	7.28	110–145	−76.8	10	90	24.0	1.0	1.4	90.5	72	1.0	2.7	1.9	1.3	28	83	5
6	s-Butyl Acetate	116.16	90%	0.860–0.866	7.18	104–130	—	16.2	85	22.8	0.8	3.6	87	77.5	1.8	2.5	1.7	1.2	23	76	6
7	Pentacetate	130.18	85% amyl acetates	0.86 –0.87	7.21	126–155	< −70	9 (30°C)	107	24.3	0.9	1.7	92–95	67	0.6	2.3	1.5	1.0	40	90	7
8	Methyl Amyl Acetate	144.21	95%	0.855–0.860	7.15	140–150	—	3.8	110	22.6	0.13	0.58	—	—	0.5	1.3	0.9	0.7	52	92	8
9	"Cellosolve" Acetate	132.16	95%	0.971–0.976	8.11	145–165	−61.7	1.2	150	28.2	23	6.5	—	—	0.2	2.1	1.0	0.7	68	90	9

TABLE 16.3.—VISCOSITY OF NITROCELLULOSE SOLUTIONS[3]

Pent-acetate	100
Butyl acetate	69
Ethyl acetate	21
Refined amyl acetate	100
Secondary butyl acetate	83
Blend 1 part pent-acetate, 1 part ethyl acetate, 2 parts butyl acetate	60

Methyl Amyl Acetate (Methyl isobutyl carbinol acetate) [$CH_3COOCH(CH_3)CH_2CH(CH_3)_2$]. Methyl amyl acetate is a colorless liquid with a mild and pleasant odor. This medium boiling solvent is used in nitrocellulose lacquer fabrication producing such advantages as blush resistance, reduction of "orange peel" in the lacquer film, and no swelling of oilbase undercoats.

Acidity (as acetic)	0.02% by wt, max
Boiling range at 760 mm	Below 140°C None Above 150°C None Not more than 5% distills below 143°C Not less than 95% distills below 148°C
Color	Water-white
Dryness	Miscible with 19 vol 60° Bé gasoline at 20°C
Purity	95% by wt, max
Specific gravity at 20/20°C	0.855 to 0.860
Weight per gal at 20°C	7.14 lbs

2-Ethyl Butyl Acetate. 2-Ethylbutyl acetate is a colorless liquid having a mild odor. It is a solvent for nitrocellulose, gums and resins, and is employed as a high-boiling solvent in lacquers.

Acidity (as acetic)	0.01% by wt, max
Color	Water-white
Specific gravity	0.875 to 0.881 at $\frac{20°C}{20°C}$
Boiling range	155°–164°C
Purity	90% min
Dryness	Miscible with 19 vols Bé gasoline at 20°C
Average weight	7.33 lbs/gal (20°C)

2-Ethylhexyl Acetate. Ethylhexyl acetate is a water-white, stable liquid. It will dissolve nitrocellulose and many of the natural and synthetic resins. It is used in slow-evaporating preparations such as brushing and dipping lacquers, mist coatings, baking finishes and lacquer emulsions.

Acidity (as acetic)	0.02% by wt, max
Purity	88 to 92%
Specific gravity	0.870 to 0.876 at $\frac{20°\mathrm{C}}{20°\mathrm{C}}$
Boiling range	
Below 190°C	Not more than 5% distills (760 mm)
Above 198°C	Not more than 2% distills (760 mm)
200°C	End point
Color	Water-white
Dryness	Miscible with 19 vols of 60° Bé gasoline at 20°C
Average weight	7.26 lbs/gal (20°C)

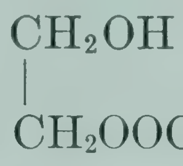
Cyclohexyl Acetate (Hexalin acetate, Hexahydrophenyl acetate, Adronol acetate) $(CH_3COO\text{—}\underbrace{CHCH_2CH_2CH_2CH_2CH_2}_{})$. Cyclohexyl acetate is a colorless, water-insoluble liquid with an odor resembling that of amyl acetate. It is miscible in all proportions with most of the lacquer solvents and diluents, with halogenated and hydrogenated hydrocarbons, and will completely dissolve waxed dammar and unrun congo copal. It is a good solvent for cellulose ethers and nitrocellulose and has powerful solvency for basic dyes, blown oils, raw rubber, metallic soaps, driers, shellac, bitumens, and a wide range of natural and synthetic resins and gums. It is used in spraying and brushing lacquers imparting blush resistance and good flow.

Boiling range	160–180°C
Color	Water-white
Flash point	64°C
Freezing point	−65°C
Purity	88–95% min
Residue	None
Refractive index	1.435–1.445
Specific gravity at 20°C	0.968–0.972
Water	None
Viscosity (S.U.V. at 100°F)	32

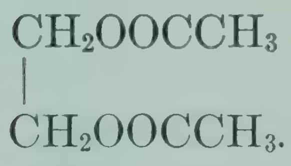
Methyl Cyclohexanyl Acetate. Methyl cyclohexanyl acetate (Sextate, methyl Hexalin acetate, hexahydrocresol acetate, hexahydromethylphenol acetate) is a colorless high boiling liquid having an ester-like odor. Its miscibility and solvent action are quite similar to those of cyclohexanyl acetate but it is slower acting. It is a solvent for nitrocellulose, basic dyes, rubber, bitumens, oils, fats and waxes, and for such resins as dammar, elemi, manila, mastic, rosin, ester gum, phenolic and vinyl resins. It will dissolve, in a lesser degree, shellac, kauri and cellulose acetate. It is used as a high-boiling solvent in nitrocellulose lacquers for both spraying and brushing purposes. Its solvency and slow rate of evaporation impart resistance to blushing and good working qualities and produce films that are smooth, homogeneous and glossy. Its dilution ratio with various diluents are as follows—

xylene	is 2.5
toluene	is 2.5
benzene	is 2.0
white spirits	is 1.5

Acidity	4.04% (max)
Ester content	80%–90%
Boiling range	175°–190°C
Flash point	66°–69°C
Specific gravity	0.95

Ethylene Glycol Monoacetate  $\begin{array}{l} CH_2OH \\ | \\ CH_2OOCCH_3 \end{array}$. Ethylene glycol monoacetate is a colorless, odorless liquid and is structurally a primary alcohol and an ester. It is made by combining a dihydric alcohol and a monocarboxylic acid. It will mix completely with water and many of the lacquer solvents. Ethylene glycol monoacetate will dissolve cellulose esters and ethers and many of the resins.

Boiling point	181°C
Specific gravity	1.109 (20°C)
Flash point	102°C

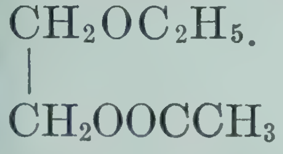
Glycol Diacetate  $\begin{array}{l} CH_2OOCCH_3 \\ | \\ CH_2OOCCH_3 \end{array}$. Glycol diacetate is a colorless liquid having a faint odor resembling that of ethyl acetate. It will dissolve a wide range of cellulose esters, camphor, dammar, ester gum, elemi, mastic, rosin and sandarac. When it is mixed with active solvents its range of solubility is increased for a wide variety of cellulose esters and ethers and for natural and synthetic resins.

Specific gravity	1.11
Boiling range	186–190°C
Refractive index	1.415

GLYCOL-ETHER ACETATES

Ethylene Glycol Monomethyl Ether Acetate (Methyl "Cellosolve Acetate") ($CH_3OCH_2CH_2OOCCH_3$). This is a colorless and odorless liquid. It is a solvent for cellulose acetate and it is used in nitrocellulose lacquers to prevent blush. It is also used in dips and cements, and in nonflammable celluloid.

Acidity (as acetic)	0.02% by wt, max
Boiling range	130 to 160° C Not more than 10% below 140°C Not more than 5% above 150°C
Color	Water-white
Toluene dilution ratio	2.5
Dryness	No turbidity with 19 vol 60 Bé gasoline
Purity	92–95%
Residue	None
Specific gravity at $15\frac{1}{2}$°C	1.003–1.013
Weight per gal	8.42 lbs



Ethylene Glycol Monoethyl Ether Acetate ("Cellosolve" Acetate) $\begin{array}{l}CH_2OC_2H_5\\ |\\ CH_2OOCCH_3\end{array}$. This is a water-white liquid with a mild, characteristic odor. It is widely used as a solvent in nitrocellulose lacquers where it imparts gloss, flow, and prevents blush.

Specifications

Acidity (as acetic)	0.02% by wt, max
Boiling range	140–165°C, at least 90% between 145–160°C
Color(APHA)	15 max
Toluene dilution ratio	2.5
Dryness	No turbidity with 10 vols 60 Bé gasoline
Purity	90% min
Residue	None
Specific gravity at 20/20°C	0.971–0.976
Weight per gal	8.08 lbs

Physical Properties

Molecular weight	132.09
Boiling point	156.2°C
Specific gravity	0.976 at $\frac{15°C}{15°C}$
Weight per gallon	8.13 (15°C)
Refractive index	1.4030 (25°C)
Surface tension	31.8 dynes/sq cm (25°C)
Viscosity	1.205 centipoises (25°C)

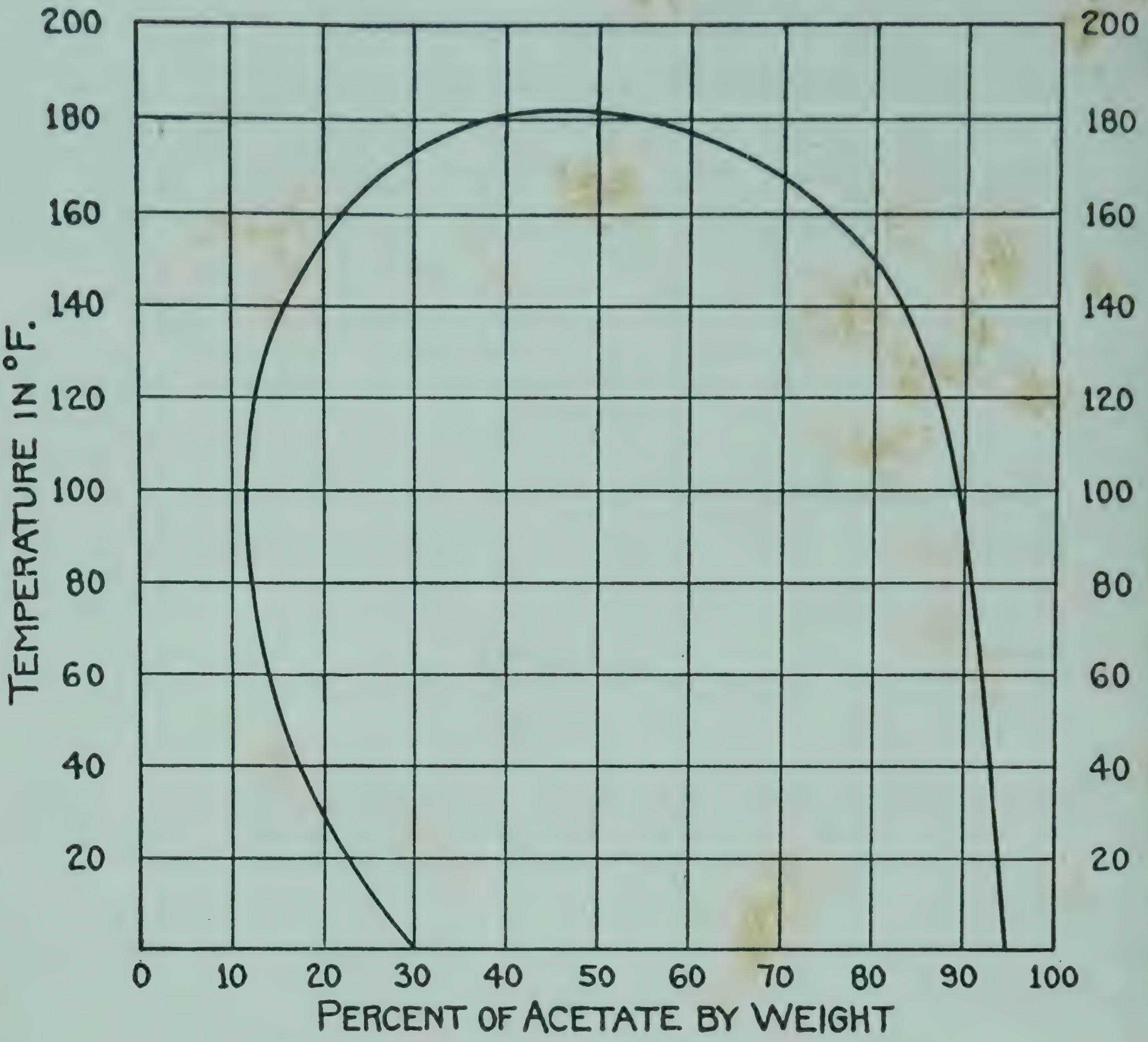


FIGURE 16.30. Solubility Curve of "Cellosolve" Acetate and Water.[1]

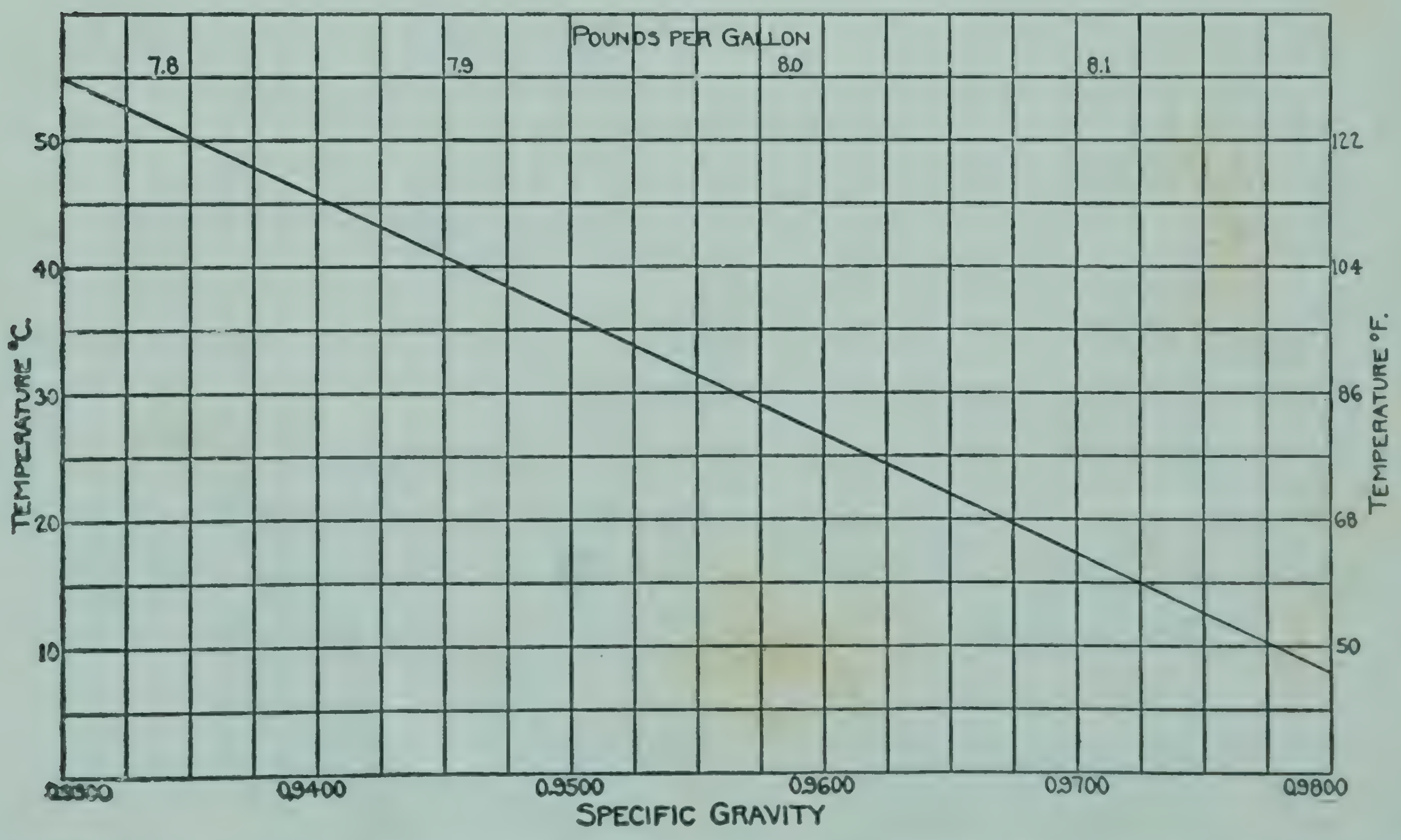


FIGURE 16.31. Specific Gravity and Weight per Gallon of "Cellosolve" Acetate at Various Temperatures.[1]

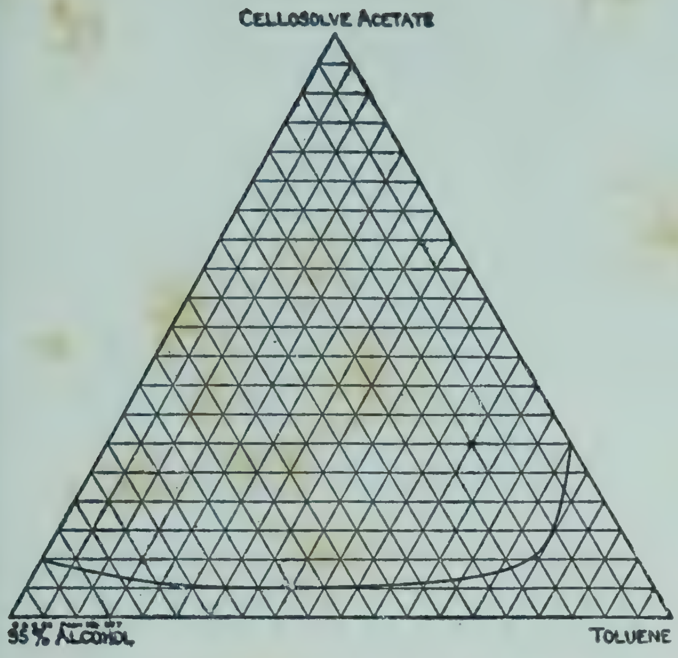


FIGURE 16.32. Solubility of $\frac{1}{2}$-Second R. S. Nitrocellulose in Mixtures of "Cellosolve" Acetate, 95% Ethyl Alcohol and Toluene.[1]

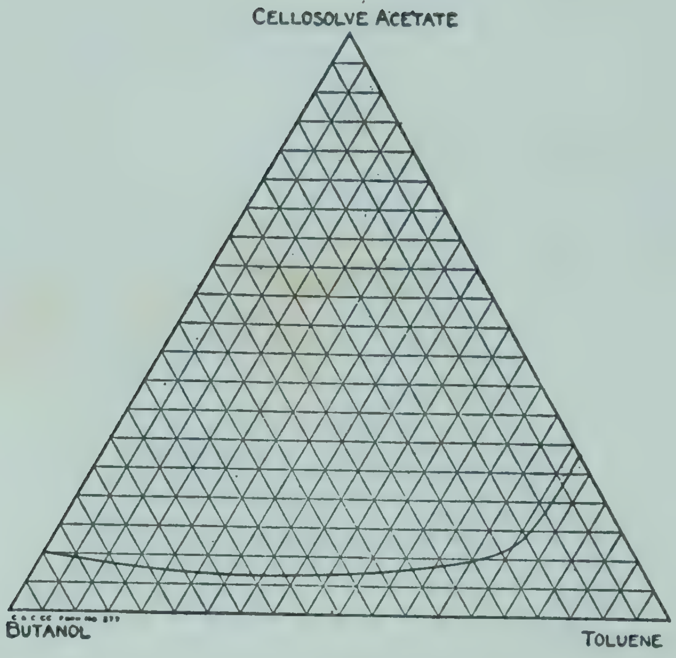


FIGURE 16.33. Solubility of $\frac{1}{2}$-Second R. S. Nitrocellulose in Mixtures of "Cellosolve" Acetate, Butanol and Toluene.[1]

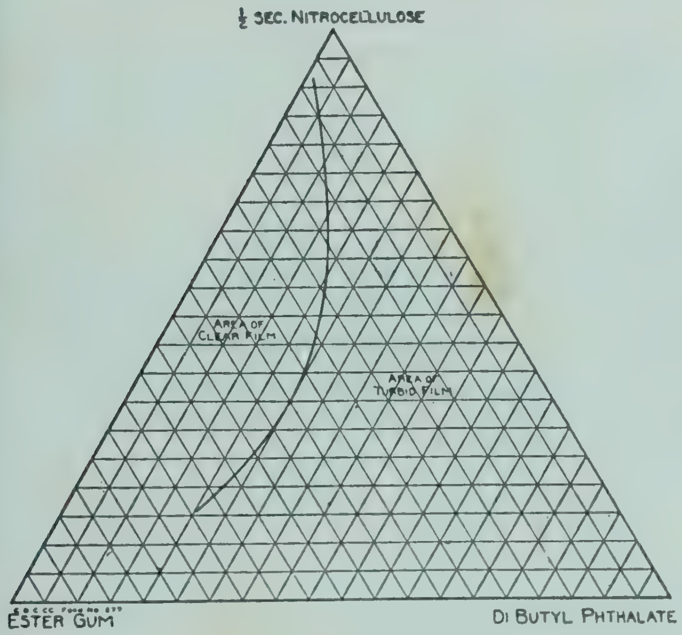


FIGURE 16.34. Compatibility of $\frac{1}{2}$-Second R.S. Nitrocellulose, Ester Gum and Dibutyl Phthalate in 50% "Cellosolve" Acetate and 50% Butanol.[1]

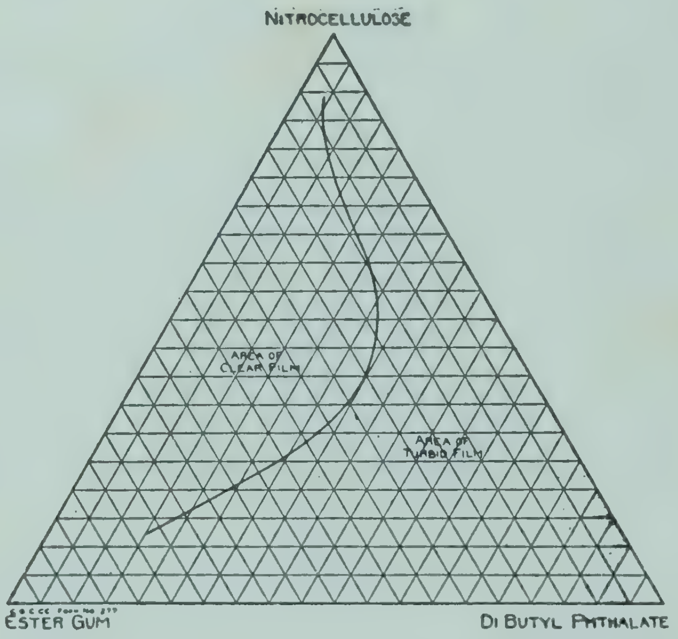


FIGURE 16.35. Compatibility of $\frac{1}{2}$-Second R.S. Nitrocellulose, Ester Gum and Dibutyl Phthalate in "Cellosolve" Acetate.[1]

Vapor pressure	2.3 mm. Hg (20°C)
Specific heat	0.494 (20°–25°C)
Flash point	55°C (131°F)
Dilution ratio	Toluene 2.6
	V.M. & P. naphtha 1.12
Electrical conductivity	2×10^{-8} recip ohm

Methoxy Butyl Acetate (Butoxyl). Methoxy butyl acetate is a high-boiling, colorless liquid of pleasant odor. It is a solvent for oils, resins, rubber, cellulose ethers and nitrocellulose. Butoxyl will tolerate high dilutions with nonsolvents.

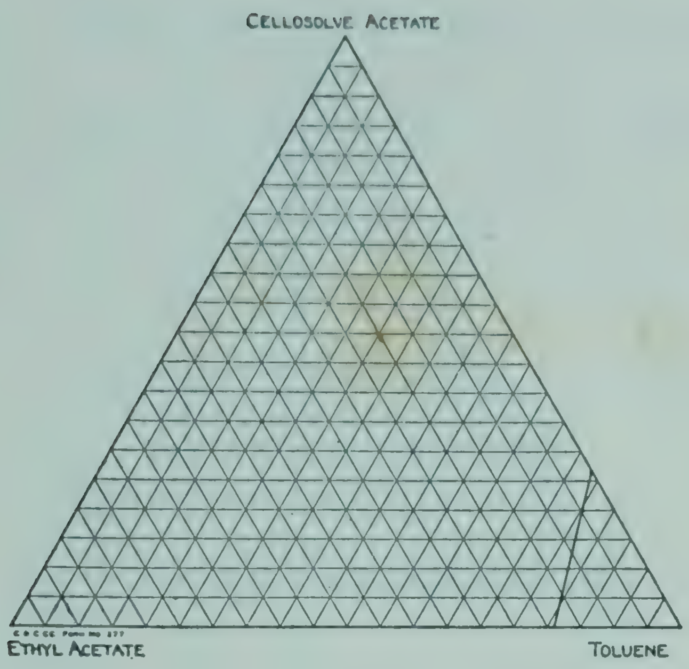


FIGURE 16.36. Solubility of ½-Second R. S. Nitrocellulose in Mixtures of "Cellosolve" Acetate, Ethyl Acetate and Toluene.[1]

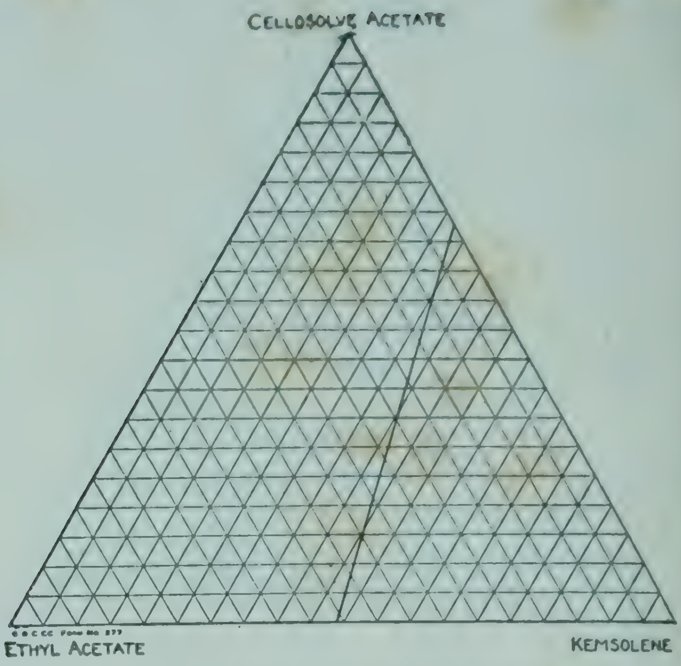


FIGURE 16.37. Solubility of ½-Second R. S. Nitrocellulose in Mixtures of "Cellosolve" Acetate, Ethyl Acetate[1] and Kemsolene.

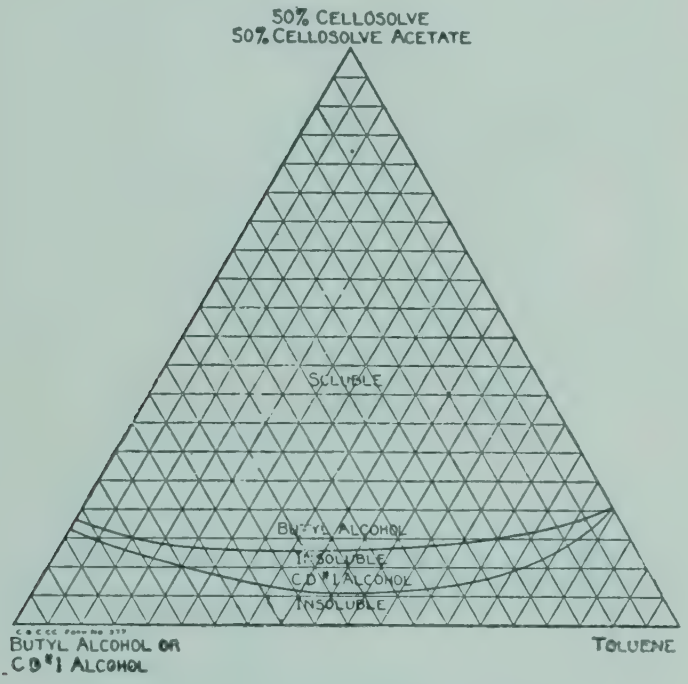


FIGURE 16.38.
Solubility of ½-Second R. S. Nitrocellulose in Mixtures of 50% "Cellosolve" —50% "Cellosolve" Acetate, Toluene, and Butanol or C. D. No. 1 Ethyl Alcohol.

PROPIONATES

The propionic esters (CH_3CH_2COOR) are very similar to the acetic esters in physical and chemical properties with the difference that the former have a higher boiling point, lower evaporation rate and a lesser power of solubility. They are miscible with many of the lacquer solvents and diluents and possess a distinctive but not a disagreeable odor. The consumption of these esters for solvent purposes is relatively small compared to the highly developed acetate esters.

Methyl Propionate ($CH_3CH_2COOCH_3$). Methyl propionate has been advocated as a solvent for cellulose derivatives. When it is admixed with other propionates (such as ethyl, propyl, butyl, and amyl) the mixture will dissolve cellulose ethers and esters.

Boiling point	91°C
Specific gravity	0.937 (4°C)

Ethyl Propionate (Propionic ether, Propionic ester) ($CH_3CH_2COOCH_2$-CH_3). Ethyl propionate is a colorless liquid with an odor resembling that of pineapples. It is a solvent for cellulose ethers and esters and for a variety of natural and synthetic resins. It is used principally as an ingredient in soft drinks and fruit syrups.

Acidity (as propionic)	0.02% by wt, max
Distillation range	90 to 100% between 80 and 120°C
Color	Water-white
Toluene dilution ratio	2.5–3.0
Dryness	No turbidity with 19 volumes gasoline
Evaporation rate	Slower than ethyl acetate
Purity	85 to 90%
Residue	None
Specific gravity at 15½°C	0.876–0.886
Weight per gal	7.35 lbs

***n*-Butyl Propionate** ($CH_3CH_2COOC_4H_9$). *n*-Butyl propionate is a water-white liquid with an apple-like odor. It is miscible with most of the lacquer solvents and diluents and with oils but not miscible with water. It is a solvent for nitrocellulose and many of the natural and synthetic resins. When an active solvent is added to it, butyl propionate will dissolve many of the cellulose esters and ethers. It may be used as a solvent in lacquer fabrication where it imparts gloss, adhesion and prevents blushing. It is also used to replace butyl and amyl acetate when lower volatility and slower evaporation are desired.

Acidity (as propionic)	0.35% by wt, max
Blush resistance at 90°F (10% ½ sec. R.S. nitrocellulose solution)	Clear 85% Relative humidity Blush 90%
Distillation range	120–175°C
Coefficient of expansion	
per 1°F	0.00060
per 1°C	0.00108
Color	Water-white
Dilution ratio	
Toluol	2.1
Petroleum naphtha	1.2
Distillation range:	
Below 120°C	None
Below 140°C	Not more than 50%
Below 150°C	Not less than 85%
Above 160°C	None

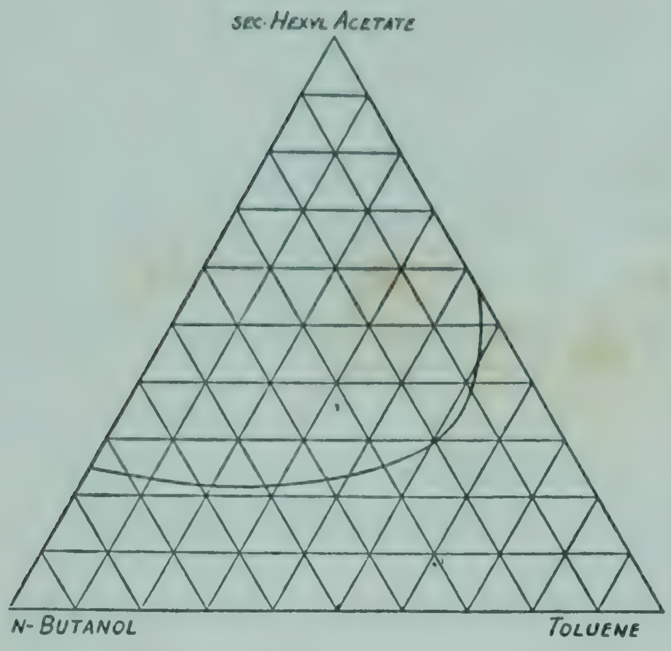


FIGURE 16.39. Solubility of $\frac{1}{2}$-Second Nitrocellulose in the System *sec*-Hexacetate-Butanol-Toluene.[4]

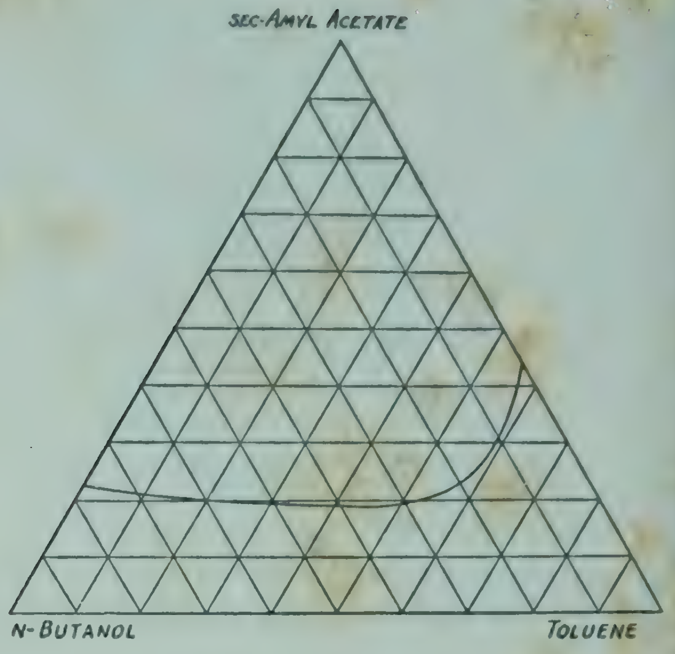


FIGURE 16.40. Solubility of $\frac{1}{2}$-Second Nitrocellulose in the System of *sec*-Amyl Acetate-Butanol-Toluene.[4]

Dryness at 20°C	Miscible without turbidity with 20 volumes 60° Bé gasoline
Evaporation rate at 95°F (in minutes)	
5%	$2\frac{1}{2}$
25%	12
50%	$24\frac{3}{4}$
75%	$41\frac{1}{2}$
90%	$56\frac{1}{2}$
95%	$63\frac{1}{4}$
Flash point	63°F
Non-volatile matter	0.005 gm/100 cc, max
Purity	90–92%
Residue	None
Solubility of water in solvent at 25°C	1.2% by vol
Specific gravity at 20/20°C	0.868–0.872
Viscosity (10% $\frac{1}{2}$ sec. R.S. nitrocellulose solution)	5.9 centipoises
Weight per gal at 20°C	7.24 lbs

Amyl Propionate ($CH_3CH_2COOC_5H_{11}$). Amyl propionate is a colorless, volatile liquid with an apple-like odor. It will dissolve cumar resins, elemi, ester gum, mastic, copal, kauri, sandarac, and nitrocellulose and it is miscible with most lacquer solvents and oils. It has a slow solvent action upon cellulose ethers thus acting as a latent solvent and this latency can be overcome when acetone or ethyl alcohol is added to it. It has similar solvent properties to amyl acetate but is not as rapid and its solutions are

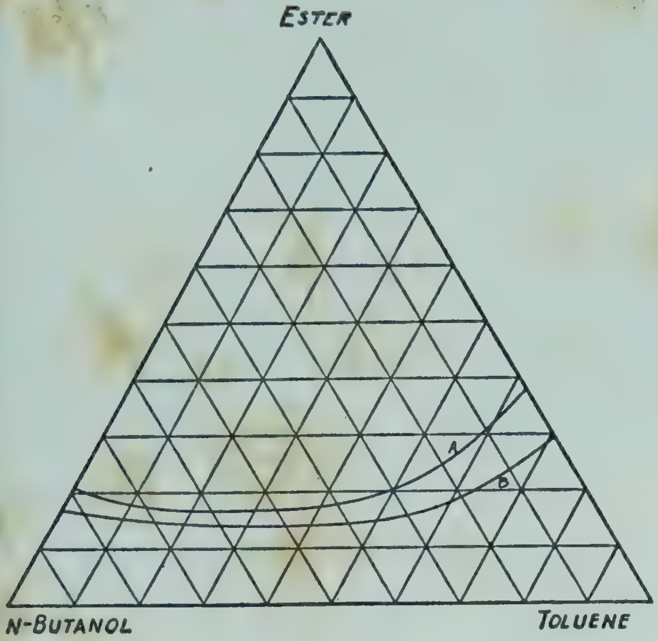


FIGURE 16.41. Solubility of ½-Second Nitrocellulose in the Systems: (*A*) *n*-Butyl Propionate-Butanol-Toluene; (*B*) *n*-Butyl Acetate-Butanol-Toluene.[4]

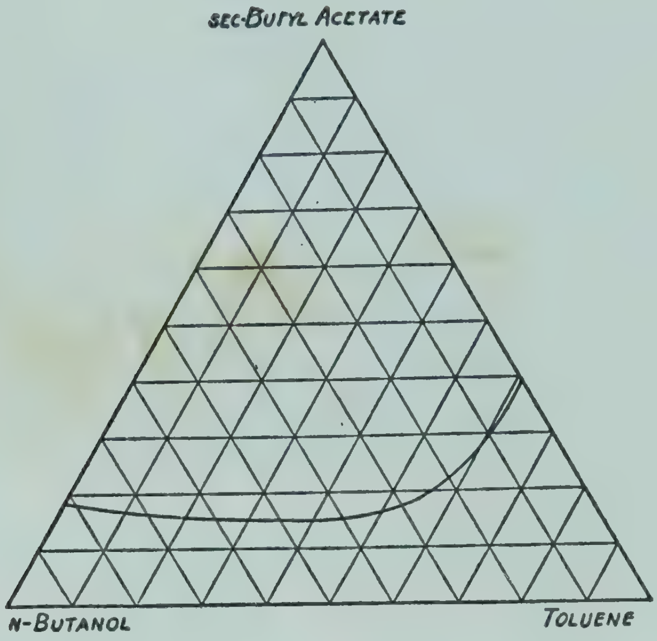


FIGURE 16.42. Solubility of ½-Second Nitrocellulose in the System *sec*-Butyl Acetate-Butanol-Toluene.[4]

more viscous, it has a slower rate of evaporation, and it has a more agreeable odor. It is used as a desirable high-boiling lacquer solvent imparting gloss, blush resistance and a reduction in "orange peel" effect. It is also used in flavoring and perfumery.

Acidity (as propionic)	0.030% by wt, max
Blush resistance at 90°F (10% ½ sec. R.S. nitrocellulose solution)	Clear 90% Relative humidity Blush 95%
Coefficient of expansion	
per 1°F	0.00060
per 1°C	0.00108
Color	Water-white
Dilution ratio	
Toluol	1.4
Petroleum naphtha	0.7
Distillation range:	
At or below 110°C	None
At or below 150°C	Not more than 40%
At or below 170°C	Not less than 90%
Above 175° C	None
Non-volatile matter	Not more than 0.005 gms per 100 cc
Residue	None
Solubility of water in solvent at 25°C	0.3% by vol
Specific gravity at 20/20°C	0.869–0.873
Viscosity (10% ½ sec. R.S. nitrocellulose solution)	106 centipoises
Weight per gal at 20°C	7.25 lbs

BUTYRATES

Butyrates do not find extensive use in the solvent industry because of their relatively unpleasant odor and higher price.

Ethyl Butyrate ($CH_3CH_2CH_2COOC_2H_5$). Ethyl butyrate is a non-toxic liquid having an odor suggestive of pineapples.

Its solvent properties lie between those of ethyl acetate and *n*-butyl acetate, and when mixed with other solvents it will dissolve cellulose esters and ethers, and many of the natural and synthetic resins. It is used in flavors.

Boiling point	120°C
Flash point	23°C
Specific gravity	0.879 (20°C)

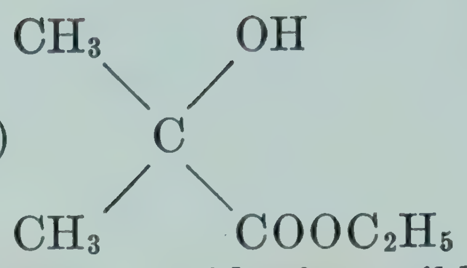
Methyl Butyrate ($CH_3CH_2CH_2COOCH_3$). Methyl butyrate is a solvent for ethyl cellulose and when it is mixed with active solvents it will dissolve nitrocellulose.

Boiling point	102°C
Specific gravity	0.898 (20°C)

***n*-Butyl Butyrate** ($CH_3CH_2CH_2COOC_4H_9$). Butyl butyrate is a water-white, neutral liquid with an apple-like odor. The commercial grade is composed of a mixture of the isomeric esters. It is a solvent for nitrocellulose, cumar resins, dammar, ester gum, elemi, shellac, and metallic resinates.

Acidity (as butyric)	0.02% by wt, max
Boiling point	156.9° C
Distillation range	95–100% between 140–170°C
Critical temperature	338°C
Toluene dilution ratio	1.8–2.0
Dryness	No turbidity with 19 vol 60° Bé gasoline Complete, standing at least 19 vols gasoline without turbidity
Flash point	51°C
Purity	90–95%
Refractive index	1.4035
Residue	None
Specific gravity at 20/20°C	0.8717
Specific heat at 20°C	0.458
Surface tension at 157°C	12.0
Vapor pressure at 20°C	113 mm Hg
Viscosity at 25°C	0.84 centipoises
Weight per gal	7.25 lbs

Ethyl Hydroxy-Iso-Butyrate (Ethyl oxybutyrate)



Ethyl hydroxy-iso-butyrate is a water-white, stable liquid of a mild odor. It is a solvent for cellulose nitrate and acetate and when mixed with other solvents it will also dissolve cellulose ethers. Its solvent action is somewhat comparable with that of ethyl lactate, differing in the following aspects:

Its solvent action is slower and requires the presence of an active solvent to accentuate it.

Its solutions of nitrocellulose are more viscous.

Its tolerance for hydrocarbons is about the same as far as it concerns nitrocellulose and is lower in the presence of acetyl cellulose.

Its volatility is higher.

Ester content	96–100%
Boiling range	142–146°C
Specific gravity	0.978–.986 (20°C)

Diethyl Carbonate [Ethyl carbonate, Diatol (contains 90% diethyl carbonate)] [$(C_2H_5)_2CO_3$]. Diethyl carbonate is a stable, colorless liquid with a mild and pleasant odor. It is miscible with alcohols, ketones, esters, aromatic hydrocarbons, some aliphatic solvents, and dissolves many of the natural and synthetic resins, nitrocellulose and cellulose ethers. Its solvent power is increased by adding either an active solvent, such as acetone or an ester, or a latent solvent such as alcohol. It has a rather low tolerance for hydrocarbons. It is used in lacquer formulation, in special lacquers for coating the cathode of radio tubes with rare earths, in organic synthesis and in the manufacture of phenobarbital.

Acidity (as carbonic)	0.02% by wt, max
Blush resistance at 90°F (10% ½ sec. R.S. nitrocellulose solution)	Clear 85% Relative humidity Blush 90%
Boiling point	180°C
Coefficient of expansion	
per 1°F	0.00066
per 1°C	0.00119
Color	Water-white
Dilution ratio	
Toluol	0.6
Petroleum Naphtha	0.4

Distillation range:	
Below 120°C	None
Below 128°C	Not less than 90%
Above 130°C	None
Dryness at 20°C	Miscible without turbidity with 20 vols 60° Bé gasoline
Evaporation rate at 95°F (in minutes)	
5%	1¼
25%	7¼
50%	14½
75%	24
90%	31¾
95%	34¾
Flash point	89°F
Freezing point	48.2°C
Non-volatile matter	Not more than 0.005 gm per 100 cc
Purity	98–100%
Solubility in water	69% by wt
Solubility of water in solvent at 25°C	1.4% by vol
Specific gravity at 20/20°C	0.973–0.977
Vapor pressure at 103°C	54 mm Hg
Weight per gal at 20°C	8.11 lbs (approx)

OXALATES

Diethyl Oxalate (Ethyl Ethanedioate) [$(COOC_2H_5)_2$]. Diethyl oxalate is a water-white liquid with a mild odor. It is used as a slow-evaporating nitrocellulose solvent, in special lacquers for fixing rare salts on the cathode of radio tubes and in organic synthesis.

Acidity (as oxalic)	0.05% by wt, max
Blush resistance at 60° F (10% ½ sec. R.S. nitrocellulose solution)	Clear 90% Relative humidity Blush
Coefficient of expansion	
per 1°F	0.00056
per 1°C	0.00101
Color	Water-white
Dilution ratio	
Toluol	3.5
Petroleum naphtha	0.7
Distillation range	
Below 180°C	None
Below 182°C	Not more than 10%
Below 188°C	Not less than 90%
Above 190°C	None
Dryness at 20°C	Miscible without turbidity with 20 volumes 60° Bé gasoline

Flash point (Open Cup)	168°F
Non-volatile matter	0.005 gm per 100 cc, max
Odor	Mild, non-residual
Purity	99% min
Specific gravity at 20/20°C	1.075–1.079
Water solubility at 25°C	10 cc solvent dissolves 1.5 cc water
Viscosity (10% ½ sec. R.S. nitrocellulose solution)	380 centipoises
Weight per gal at 20°C	8.96 lbs (approx)

Dibutyl Oxalate ($C_4H_9OOCCOOC_4H_9$). Dibutyl oxalate is a high-boiling, water-white liquid with a mild odor and having a tendency to hydrolyze and split off oxalic acid. It is miscible with most alcohols, ketones, oils, and hydrocarbons and is a solvent for benzyl abietate, cellulose esters and ethers, cumar resins, ester gum, copal ester, glyptol resins, and mastic. It is used in nitrocellulose lacquers as a plasticizing solvent, for the purpose of fixing rare-earth salts on cathode elements, and in organic synthesis.

Acidity (as oxalic)	0.05% by wt, max
Blush resistant at 90°F (1.0% R.S. ½ sec. nitrocellulose solution)	Clear 90 Relative humidity Blush
Coefficient of expansion	
per 1°F	0.00053
per 1°C	0.00095
Color	Water-white
Dilution ratio	
Toluol	2.3
Petroleum naphtha	1.0
Distillation range:	
Below 240°C	Not more than 5%
Below 248°C	Not less than 90%
Above 255°C	None
Dryness at 20°C	Miscible without turbidity with 20 volumes 60° Bé gasoline
Freezing point	−30.0°C
Non-volatile matter	0.005 gm/100 cc, max
Solubility of water in solvent at 25°C	0.5% by vol
Specific gravity at 20/20°C	0.989–0.993
Viscosity (10% ½ sec. nitrocellulose solution)	800 centipoises
Weight per gal at 20°C	8.24 lbs

Diamyl Oxalate ($C_5H_{11}OOCCOOC_5H_{11}$). Diamyl oxalate is a colorless, oily liquid miscible with most lacquer solvents, oils and hydrocarbons. It is a solvent for ester gum, copal ester, cumar resins, alkyd resins, mastic, nitrocellulose, and shellac. It is used as a plasticizer and in paint and varnish removers. Like other oxalates, it has a tendency to hydrolyze.

Boiling point	265°C
Flash point	116°C
Specific gravity	0.97

FORMATES

Methyl Formate ($HCOOCH_3$). Methyl formate is a colorless flammable liquid with a pleasant ethereal odor. It will dissolve cellulose ethers and esters but will dissolve them more readily when mixed with other solvent esters or the less volatile halogenated hydrocarbons. Mork[8] is of the opinion that methyl formate is a more powerful solvent for cellulose derivatives than acetone. It is more powerful than the other volatile formic esters when used as a fumigant and larvicide in the treatment of tobacco, dried fruit, cereals, etc.

Acidity	Neutral to methyl orange (methyl formate hydrolyzes in presence of water)
Boiling point	31.8° C
Color	Water-white
Distillation range	Below 31.5°C None Above 35.0°C None
Electrical conductivity at 25°C	3.6×10^{-5} reciprocal ohms
Flash point	−32°C
Melting point	−99.8°C
Odor initial	Pleasant, ethereal
Odor residual	Non-residual
Purity	95% to 100% ester, by wt
Refractive index at 20°C	1.3431
Solubility in water at 20°C	30% by vol
Solubility of water in solvent at 25° C	24% by vol
Specific gravity at 20/20°C	0.950 to 0.980
Vapor pressure	
0°C	195.0 mm of Mercury
10°C	309.4 mm of Mercury
16°C	400.0 mm of Mercury
20°C	476.4 mm of Mercury
25.8°C	600.0 mm of Mercury
30°C	707.9 mm of Mercury

Ethyl Formate (Formosol) ($HCOOC_2H_5$). Ethyl formate is a water-white, highly volatile and unstable liquid with a pleasant odor resembling peach kernels. It is partly soluble in water and miscible with benzene. It is a powerful solvent for cellulose nitrate and acetate, yielding solutions of unusual low viscosity which have a tendency to chill. It is an important fumigant and larvicide for the treatment of tobacco, cereals, dried fruit and similar products. It is used as a chemical intermediate in the manufacture of such medicinals as sulfadiazine, thiamin (Vitamin B_1), and perfumes and synthetic flavors.

Acidity	Neutral to methyl orange (it hydrolyzes in the presence of water)
Boiling point	54.3°C
Color	Water-white
Distillation range	51°–55°C
Electrical conductivity at 25°C	Less than 1.45×10^{-9} recip ohms
Flash point	−19°C
Freezing point	−80.5°C
Purity	95% to 100%
Refractive index at 20°C	1.3604
Specific gravity at 20/20°C	0.900 to 0.930
Solubility in water at 20°C	10% by vol
Solubility of water in solvent at 20°C	17% by vol
Vapor pressure at 20.6°C	200 mm of Hg
at 30.2°C	300 mm of Hg
Weight per gal at 68°F	7.61 lbs

Butyl Formate ($HCOOCH_2CH_2CH_2CH_3$). Butyl formate is a colorless liquid, miscible with alcohols, ethers, oils, hydrocarbons and so forth. It will dissolve cellulose nitrate, some types of cellulose acetate, and many cellulose ethers. Butyl formate will also dissolve many natural and synthetic resins such as copals, dammar, elemi, mastic, shellac, cumar resins, ester gum and alkyds in the presence of ethyl alcohol. It is used as an intermediate and in perfumes.

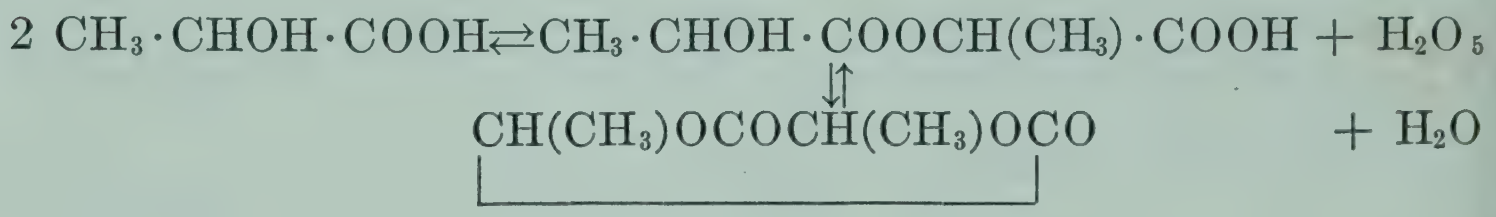
Acidity	0.02% max
Ester content	85% min
Boiling range	96–110°C
Specific gravity	0.885–0.9108

Amyl Formate ($HCOOC_5H_{11}$). Commercial amyl formate is an anhydrous, colorless liquid composed of a mixture of isomeric amyl formates with the isoamyl formate in predominance. This mixture is miscible with oils, hydrocarbons, alcohols, ketones and so forth. It is a solvent for cellulose esters, cumar, copal, gum esters, etc. It is able, when mixed with an alcohol, to dissolve shellac and alkyd resin. It is a less odoriferous and more energetic solvent than amyl acetate. It also has both a lower boiling point and a greater speed of evaporation. *n*-Butyl acetate and amyl formate have similar volatility and have substantially the same solvent power which permit free interchange of these only as far as these properties allow.

Acidity	0.05% max
Boiling point	130.4°C
Boiling range	110–130°C
Flash point	80°F
Specific gravity	0.880–0.885

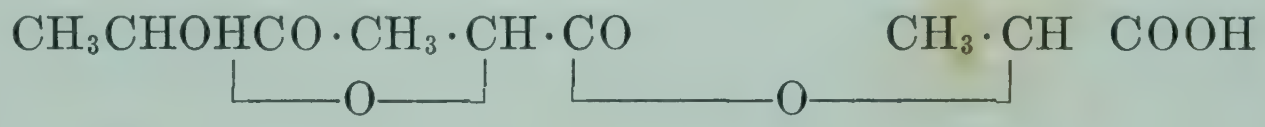
LACTATES

After studies have been made by Eder and Kutter[7] on commercial lactic acid, they find it to be a mixture of alphahydroxypropionic acid, lactyllactic acid, and water. Watson[5] has found, that when a dilute lactic acid solution is concentrated, a molecule of water is split off from two molecules of lactic acid thus forming lactyllactic acid.



$$\begin{array}{l} 2\,\mathrm{CH_3\cdot CHOH\cdot COOH} \rightleftarrows \mathrm{CH_3\cdot CHOH\cdot COOCH(CH_3)\cdot COOH} + \mathrm{H_2O}_5 \\ \qquad\qquad\qquad\qquad\qquad \upharpoonleft\!\downharpoonright \\ \qquad\qquad\qquad \underbrace{\mathrm{CH(CH_3)OCOCH(CH_3)OCO}}_{} \qquad\qquad + \mathrm{H_2O} \end{array}$$

By further concentration, one molecule of lactyllactic acid loses a molecule of water forming a lactide.



$$\mathrm{CH_3CHOH}\underbrace{\mathrm{CO\cdot CH_3\cdot CH}}_{\mathrm{O}}\cdot\underbrace{\mathrm{CO} \qquad\qquad \mathrm{CH_3\cdot CH}}_{\mathrm{O}} \quad \mathrm{COOH}$$

Chain polylactyllactic acids are also formed by the loss of a molecule of water between the alcohol and carboxyl groups. These reactions are reversable when diluted with water. The composition of lactic acid solutions are dependent upon age, temperature, concentration, and the method of preparation.

Because of the two active hydroxyl groups present in the lactic acid molecule, there are three types of esters. A number of lactic acid esters have been prepared by Smith and Claborn[6] who give their physical properties in Table 16.4.

Methyl Lactate [$CH_3CH(OH)COOCH_3$]. Methyl lactate is a water-white liquid, completely miscible with water and most organic liquids. It is a solvent for nitrocellulose, cellulose acetate, cellulose acetobutyrate, and cellulose acetopropionate. It is used in the manufacture of lacquers and dopes where it contributes high tolerance for diluents, good flow, and blush resistance.

TABLE 16.4.—PHYSICAL PROPERTIES OF LACTATES

	B.P.		SP. GR.	REFRACTIVE INDEX	SAPONIFICATION VALUE	
	°C	Mm.			Calcd.	Found
			Lactic Esters			
Methyl	144.8	760	d^{19} 1.0898	n_D^{25} 1.4132[b]		
Ethyl	154.5	760	d^{19} 1.0308	n_D^{25} 1.4121[b]		
n-Propyl	86	40	d^{20}_{20} 0.996	n_D^{25} 1.4167[b]		
Isopropyl	166–8	760	d^{20}_{20} 0.998	n_D^{25} 1.4082[b]		
n-Butyl	185	760	d^{20}_{20} 0.973	n_D^{25} 1.4214[b]		
Isobutyl	96	40	d^{20}_{20} 0.971	n_D^{25} 1.4183[b]		
sec-Butyl[c]	180	760	d^{20}_{20} 0.974			
n-Amyl	112	40	d^{20}_{20} 0.952	n_D^{25} 1.4254[b]		
Isoamyl	82	7	d^{25}_{25} 0.9614	n_D^{25} 1.4240	350	353
n-Hexyl	75	2	d^{25}_{25} 0.9533	n_D^{25} 1.4290	322	322
2-Ethyl butyl	104	12	d^{25}_{25} 0.9615	n_D^{25} 1.4307	322	321
2-Ethyl hexyl	112	3.6	d^{25}_{25} 0.9405	n_D^{25} 1.4358	277	278
Lauryl	150–3	4	d^{25}_{25} 0.9108	n_D^{25} .14433	217	212
Phenyl ethyl	124	4	d^{25}_{25} 1.0979	n_D^{25} 1.5073	289	293
Glycol[d]	140	10	d^{25}_{25} 1.1967	n_D^{25} 1.4452	419	413
Glycerol[d]	175–80[e]	2				
Benzyl	134	4	d^{20}_{4} 1.1355	$n_D^{23.5}$ 1.5049		
Stearyl	180[e]	2				
			Acetoxypropionate Esters			
Methyl	171.5	760	d^{20}_{4} 1.088	n_D^{20} 1.4111		
Ethyl	177	733	d^{17} 1.0458	n_D^{25} 1.4085[b]		
n-Propyl	195–6	766	d^{25}_{25} 1.0163	n_D^{25} 1.4123		
Isopropyl	182–3	765	d^{25}_{25} 0.9920	n_D^{25} 1.4058		
n-Butyl	213–4	767	d^{20}_{4} 1.0001	n_D^{20} 1.4147		
Isobutyl	205	763	d^{25}_{25} 0.9952	n_D^{25} 1.4140		
n-Amyl	226–7	763	d^{25}_{25} 0.9822	n_D^{25} 1.4199		
Isoamyl	221–2	763	d^{25}_{25} 0.9838	n_D^{25} 1.4190		
n-Hexyl	135	17	d^{25}_{25} 0.9770	n_D^{25} 1.4232	519	519
2-Ethyl butyl	127	14	d^{25}_{25} 0.9822	n_D^{25} 1.4245	519	522
2-Ethyl hexyl	145	13	d^{25}_{25} 0.9629	n_D^{25} 1.4298	460	462
Lauryl	165	4	d^{25}_{25} 0.9304	n_D^{25} 1.4373	373	370
Phenyl ethyl	139	4	d^{25}_{25} 1.0983	n_D^{25} 1.4896	475	476
Acetoxyethyl (glycol monolactate diacetate)	145	10	d^{25}_{25} 1.1489	n_D^{25} 1.4297		
Benzyl	145.8	4	d^{20}_{4} 1.1227	n_D^{21} 1.4874		
Glycerol monolactate triactetate[c]						

[a] Where no reference is given, the properties were determined by the authors.

[b] Properties not given in the reference but determined by the authors.

[c] Compounds not prepared by authors.

[d] Monolactate.

[e] Decomposed.

Acidity (as lactic)	0.15% by wt, max
Boiling point	144.8°C
Color	Water-white
Distillation range:	
Below 115°C	None
Between 141°C and 145°C	Not less than 60%
Above 155°C	None
Flash point	51.7°C
Heat of combustion	4778 calories per gram
Freezing point	Approx 66°C
Non-volatile matter	0.01 gram per 100 cc, max
Purity	95% min
Refractive index at 20°C	1.4131
Specific gravity at 20/20°C	1.087 to 1.097
Water at 20°C	No turbidity when mixed with 19 volumes of 60° Bé gasoline
Weight per gal at 68°F	9.09 lbs

Ethyl Lactate [$CH_3CH(OH)COOC_2H_5$]. Ethyl lactate is a colorless and almost odorless liquid, which, upon evaporation, will sometimes develop a disagreeable odor. This is owing to the lactides, or inner anhydrides, contained in the lactic acid made by fermentation. It is miscible with water, alcohols, ketones, esters, hydrocarbons, and oils.

Ethyl lactate will dissolve cellulose acetate and nitrate and many of the ethers of cellulose. It is also a solvent for basic dyes, alkyd resins, kauri, manila, pontianac, rosin, shellac, vinyl resins.

Ethyl lactate has high solvent power and equally high tolerance for non-solvents and diluents. These exceptional properties are accounted for by the existence of both an alcohol and an ester group in its molecule.

Its rate of evaporation is slow but this is desirable for brushing lacquers. The presence of ethyl lactate in a solvent mixture imparts good working-qualities and good flow, and permits the application of a thin coat on almost any surface. The resulting films are smooth and uniform, although at times the film will remain soft for a longer period than is anticipated. Its solvent action is slower than that of butyl or amyl acetate and the resulting solution has a high viscosity. However, it will tolerate two or three times as much non-solvent or diluent. In fact, a solution of pyroxylin in ethyl lactate will tolerate the addition of 25 per cent water without precipitation. As far as water tolerance is concerned it has no rival in the field of solvents.

Ethyl lactate is useful as a lacquer solvent for cellulose nitrate, acetate and ethers. It is used in the preparation of stencil sheets, incandescent mantle lacquers, in laminated glass.

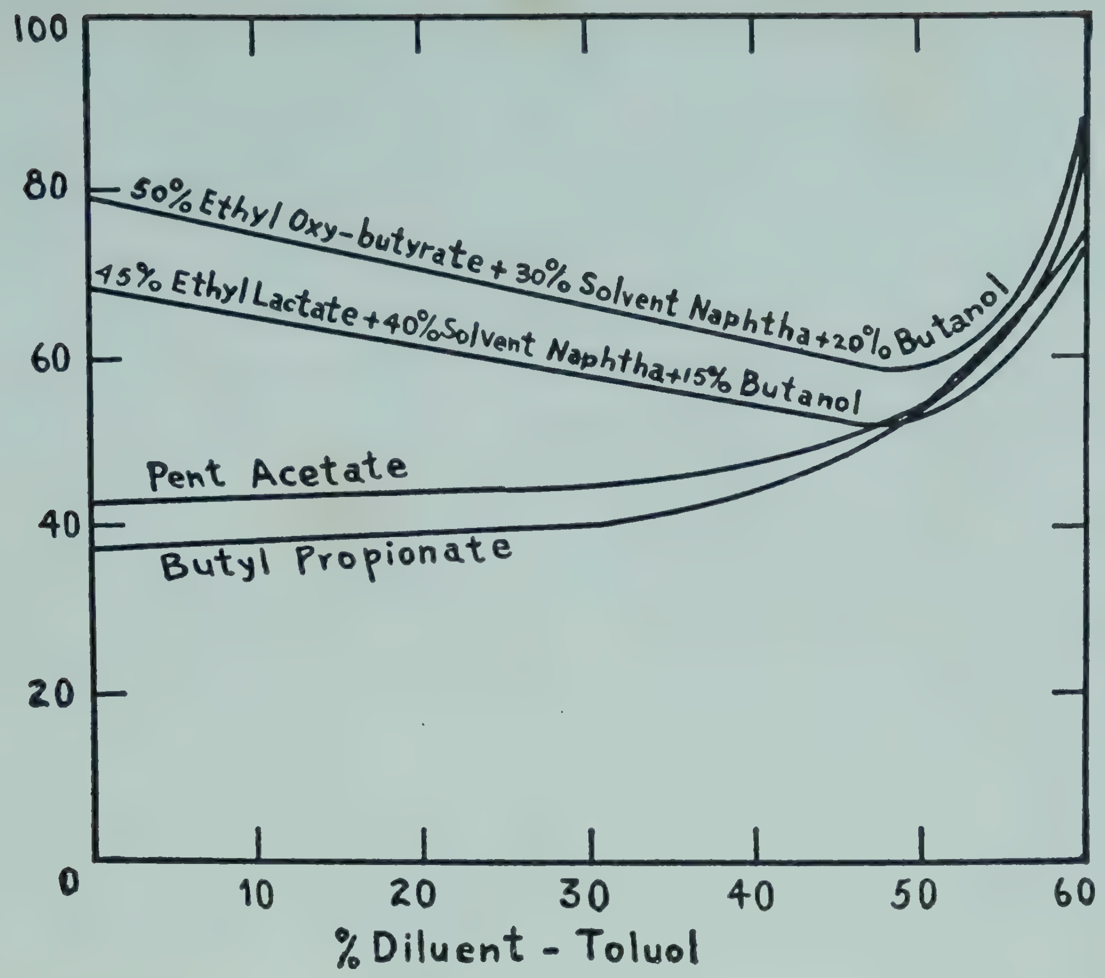


FIGURE 16.43. Viscosity Curves of 10-Per Cent Nitrocellulose Solutions.[3]

Physical Properties and Specifications

Acidity (as lactic)	0.08%, max
Color	Water-white
Distillation range:	
Below 102°C	None
Below 139°C	Not more than 10%
Below 155°C	Not less than 90%
Above 173°C	None
Dryness	Miscible without turbidity with 20 vols 60° Bé gasoline at 20°C
Non-volatile matter	0.005 g/100 cc, max
Odor	Mild, non-residual
Purity	96% min
Specific gravity at $\frac{20^\circ C}{20^\circ C}$	1.020–1.036
Blush resistance at 90°F (10% $\frac{1}{2}$-sec. R.S. nitrocellulose sol.)	Clear 80% Relative humidity Blush 85%
Coefficient of expansion	0.00058/1°F 0.00104/1°C
Dilution ratio	5.5 with toluene 0.8 with petroleum naphtha
Evaporation rate at 95°F	
Per cent	5 25 50 75 90 95
Minutes	4 23 $47\frac{3}{4}$ 73 $92\frac{3}{4}$ 101
Flash point	129°F. (approx)
Viscosity (10% $\frac{1}{2}$-sec. R.S. nitrocellulose solution)	195 centipoises
Water solubility	Soluble in all proportions (25°C)

Butyl Lactate [$CH_3CH(OH)COOC_4H_9$]. Butyl lactate is a colorless liquid having a mild odor. The commercial grade contains condensation products and its physical and chemical properties will vary. It is miscible with many of the lacquer-solvents, diluents and oils. It will dissolve such substances as cellulose esters, cumar resins, ester gum, copal ester, alkyd resins, mastic and shellac. It has a high tolerance for non-solvents and it evaporates slowly. Its presence in a solvent mixture will impart brilliance, gloss, adhesion, flexibility and tenacity to the film. It is used as a solvent in lacquers, in stencil manufacture and in lithographic and printing inks. It is also used as an anti-skinning agent, as an intermediate, and in perfumes.

Purity	95% ester by wt, min
Specific gravity at $\frac{20°C}{20°C}$	0.974 to 0.984
Acidity (as lactic)	0.15% max
Water	No turbidity when mixed with 19 vols of 60° Bé gasoline at 20°C
Non-volatile matter	0.01 g per 100 cc, max
Color	Water-white
Distillation range	
Below 140°C	None
Between 155°C and 195°C	Not less than 60 per cent
Between 187°C and 189°C	Not less than 90 per cent
Dry point	Not above 200°C
Molecular weight	146.11
Odor	Mild (No residual odor)
Flash point	71°C (159.8°F)
Freezing point	−43°C
Weight per gallon	8.15 lbs. (68°F)
Solubility in water	3.4% by vol (25°C)
Solubility of water in butyl lactate	13.0% by vol (25°C)
Refractive index	1.42162 (20°C)
Vapor pressure	0.4 mm Hg (20°C)
Heat of vaporization	77.4 cal/g (20°C)

Amyl Lactate [$CH_3CH(OH)COOC_5H_{11}$]. Amyl lactate is a colorless to pale yellow non-toxic liquid with an odor like that of brandy. Its composition varies containing lacticides among other things. It is miscible with alcohols, ketones, esters, hydrocarbons, oils, and so forth. It is a solvent for cellulose ethers, cumar resins, copal esters, mastic, nitrocellulose, and shellac, and will dissolve alkyd resins when combined with alcohol. It is used as a plasticizer for cellulose derivatives.

Acidity (as lactic)	0.05% by wt, max
Color	Water-white
Distillation range at 20 mm	100% between 75–150°C
Flash point	175°F
Purity	At least 95%, min
Specific gravity at 20°C	0.954–0.966
Weight per gal	7.99 lbs

SILICON ESTERS

Ethyl Silicate (Silicon tetraethyl ester, Ortho-Silicic acid ethyl ester) [$Si(OC_2H_5)_4$]. Ethyl silicate is a water-white liquid, soluble in alcohol. It hydrolyzes in water to an adhesive form of silicic acid and alcohol. It is used in lacquers and paint as a pigment binder giving films that are resistant to fire and chemicals and are weatherproof. A less pure, higher silica ester, Ethyl Silicate 40, is also available commercially.

Specifications—Tetraethyl Silicate

Acidity (as HCl)	0.05% by wt, max
Available silica (as SiO_2)	28.8%
Boiling point	165.5°C
Boiling range at 760 mm	
Below 160°C	Not more than 5%
Below 170°C	Not less than 95%
Color	Water-white
Purity	97%, min
Specific gravity at 20/20°C	0.933 to 0.938
Weight per gal at 20°C	7.78 lbs

Specifications—Ethyl Silicate

Acidity, maximum acidity (as HCl)	0.1%
Available silica (as SiO_2)	34–42%
Boiling point	165°C
Boiling range at 760 mm	
Below 80°C	None
Below 110°C	Not more than 5%
Color	Light brown
Odor initial	Mild
Specific gravity at 20/20°C	1.050 to 1.070
Weight per gal at 20°C	8.82 lbs

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